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# QUANTITATIVE ANALYSIS

WITH APPLICATIONS TO

# AGRICULTURAL AND FOOD PRODUCTS

BY

HOWARD O. TRIEBOLD, PH.D.

*Professor of Agricultural and Biological Chemistry,*
*Pennsylvania State College*

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To

My Mother

MARY TRIEBOLD

# PREFACE

There is a growing demand for students in agricultural curricula (agronomy, dairy manufacturing, horticulture, pre-veterinary, soils, etc.), as well as students in food and nutrition curricula, to acquire training in the fundamentals of quantitative analysis with sufficient laboratory techniques to equip them for control and research work in these various specialized fields. Usually these curricula do not contain the prerequisites or allow sufficient time for the students to take a standard course in quantitative analysis. If such a course is taken, an objection is frequently raised that very little emphasis is placed on the analysis of products in which the students are interested. To meet the demands and interests of such students has been one of the objects of this book.

There are students majoring in Agricultural and Biological Chemistry, who have had a good fundamental course in quantitative analysis. They should receive further training in the techniques and methods most generally used in their field. Methods of analysis for the various types of agricultural and food products should be provided so that a well-rounded training is obtained. The needs of this group of students have been considered in preparing this book.

Students, and research workers as well, are frequently handicapped in making an analysis by having only a set of directions available with no discussion of principles involved. Anyone with training in analytical techniques can blindly follow a "cook book" procedure. However, a good student or research worker will not be satisfied until the principle underlying the method is understood. Then the method becomes clear and forms a part of the analyst's experience as he progresses in his field. This too has been considered in the preparation of this book.

For several years, the author has used mimeographed sets of notes and laboratory exercises in an elementary course and also in an advanced course in agricultural quantitative analysis. This mimeographed material was used as a nucleus for this book.

Parts I, II, and III are designed to give the student the fundamentals of quantitative analysis. Sufficient laboratory exercises are included with the text material to develop proper techniques as the student progesses. Whenever possible, methods of analysis involving agricultural or food products are used. Students in advanced courses and research workers will also have an interest in some of this fundamental material.

Physical chemical methods are being used more and more extensively in quantitative analysis. A number of these methods are discussed in Part IV. An attempt has been made to explain the principle underlying each of these methods in simple terms. Instructions in the use of these methods are also given. This section is of special interest to the advanced students and research workers.

Since agricultural and food products consist primarily of carbohydrate, protein, fat, mineral matter and moisture, methods for the analysis of these constituents should be emphasized. Part V, then, considers the general methods for the analysis of the common constituents of agricultural and food products. Whenever possible, all the generally accepted methods are given in detail. This permits a comparison of the available methods and the selection of one for a particular sample or condition. In each instance, the principle of the method is explained thoroughly and the "whys" and "wherefores" of the procedure given.

Part VI deals with the methods of analysis for a number of agricultural and food products. The products selected are not necessarily the most important economically or most widely used. They do, however, represent a cross section of the type of products met with in agricultural and food analysis. So, for example, if one is familiar with the analysis of butter fat, one can also apply these same techniques to any other fat; the same may be said for maple syrup with respect to sugar products in general, etc. Some of these methods can well be used in an elementary course while others are primarily for advanced work in quantitative analysis. The principle of each method is stated together with detailed instructions and explanations.

In addition to understanding the principle of a method and acquiring the technical skill necessary in performing the actual analysis, it is also necessary to use the data obtained for making certain calculations. Thus the student should have training in the solution of problems, especially those that he will use most frequently and which are of a practical nature. In Part VII, the author has attempted to explain certain types of problems that are used frequently in quantitative analysis. A number of problems are then stated, starting with the simpler ones and following the general order of subject matter in the text. Thus there are problems given for all the types of analyses discussed.

In general, the book considers all the phases of quantitative analysis that are usually included under that subject. However, instead of making the applications to strictly inorganic substances, the applications have been made, insofar as possible, to agricultural and food products.

In addition to the help derived from standard textbooks on Quantitative Analysis and Food Analysis in the preparation of this book, the author wishes to acknowledge his indebtedness to the Association of Official Agricultural Chemists for their permission to use certain tables and methods found in their Book of Methods of Analysis. Grateful acknowledgment is also accorded to: Bausch and Lomb, Burrell Technical Supply Co., Christian Becker, Fisher Scientific Co., La Motte Chemical Products Co., and Leeds and Northrup Co., for the loan of electrotypes and permission to use certain cuts for illustrative purposes.

The author is also indebted to his friends and associates who have aided him by encouragement and advice; especially the helpful advice of Dr. M. W. Lisse in organizing the subject matter dealing with hydrogen-ion concentration, and Dr. P. M. Althouse for making the necessary drawings.

HOWARD O. TRIEBOLD

STATE COLLEGE, PA.
1946

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# PART I

# FUNDAMENTALS OF QUANTITATIVE ANALYSIS

## CHAPTER I

## INTRODUCTION TO QUANTITATIVE ANALYSIS

Analytical chemistry, one of the oldest branches of chemistry, has maintained its importance to the present time. Our industries have developed to their present state largely through the help of analytical chemistry. Experimental research, in all of its various fields, has made rapid progress only because suitable analytical methods were available to determine and check the composition of substances or the progress of reactions. For example, the synthesis of certain of the vitamins and hormones has been accomplished only after their composition was established by analytical procedures.

The object of analytical chemistry is to determine what substances are present in an unknown material (qualitative analysis), and exactly how much of each substance is present (quantitative analysis). In the investigation of an unknown material, obviously a qualitative must precede a quantitative analysis to determine what substances are present, so that the proper analytical procedures may be used. In agricultural analysis, the various components of the material analyzed are usually well known hence it is simply a matter of determining the percentage of each component present. This requires a thorough knowledge of analytical methods so that the proper procedures may be selected for the material in question.

In the analysis of a material for its content of a certain component, three general quantitative methods present themselves: gravimetric, volumetric, and physical chemical methods. Of these, the two most important in elementary quantitative analysis are the gravimetric and volumetric methods. As the names imply, the first is concerned mainly with weights and the second mainly with volumes. This relationship is made clearer if we consider the analytical determination of chloride in a soluble chloride. The sample could be treated with an excess of silver nitrate to precipitate all the chloride as insoluble silver chloride. This precipitate could then be filtered off, washed, dried, weighed, and the amount of chloride calculated. This would be a gravimetric analysis. On the other hand, the sample could be put into solution and only sufficient silver nitrate solution added to precipitate all the chloride. Then from the volume of silver nitrate solution used, and its concentration, the amount of chloride could be calculated. This would constitute a volumetric analysis.

Physical chemical methods involve the determination of a substance by the measurement of certain physical properties such as index of refraction, rotation of a plane of polarized light, specific gravity, color, etc. These specialized methods will be considered in detail in Part IV.

In the successful prosecution of a quantitative analysis, it is essential that the principle underlying the determination be understood and mastered before attempting the actual determination. Unless this is done, the analyst follows a "cook book" procedure from which he gains little or no knowledge and runs into the possibility of serious error due to the lack of understanding of the determination. Thus it is advisable to study all determinations carefully previous to the laboratory period, so that any questionable points may be cleared up before the actual analysis is initiated.

**The Notebook—A Record of Data.** The notebook is the diary of the analytical chemist since in it should be a record of all the work performed. In order that this may hold true, *all data must be recorded in permanent form as soon as they are obtained.* This is accomplished by *immediately entering all data in ink in a bound notebook.* No erasing of data is permitted and any necessary corrections should be made without destroying the original entries.

Several objectives are gained by this procedure:

1. The loss of data recorded on scraps of paper, etc., which are later lost or mislaid is eliminated. All data on a particular experiment are systematically located in one place.

2. The temptation to be dishonest by falsifying results is, to a large extent, eliminated since the data cannot readily be changed once they are recorded. The necessity for absolute honesty in analytical work cannot be overemphasized. *Honesty is the prime prerequisite of the quantitative analyst.* The values obtained in an analysis are only of value to the degree that they represent the true results obtained after careful completion of a systematic scheme of analysis.

3. Some apparently unimportant data at the time are recorded which, at a later date, may prove to be highly important. This fact has been proven time after time in research work.

4. The systematic organization of data in a notebook makes it possible to check easily for possible errors in the determination. Many times the repetition of an experiment is avoided by finding errors made in the calculations, etc. If there has been an error in technique, the data will frequently show where the error has been made, thus preventing its repetition in a subsequent analysis.

The material recorded in the notebook should be organized so that anyone familiar with the subject can easily understand and interpret it. To accomplish this, and to insure uniformity in the individual reports, a certain set procedure for recording data should be established. Both the right-hand and left-hand pages of a notebook should be reserved for a single experiment. The right-hand page should contain the sample number, a statement of the principle involved in the determination, all the data obtained in the experiment, and the result of the analysis. The following illustrates a typical right-hand page in a notebook:

**Determination of Sulfur in a Soluble Sulfate**

Date started.............
Sample No. 125 Date completed..........

Principle: An accurately weighed sample is dissolved in water and the sulfur precipitated as insoluble $BaSO_4$ by the addition of an excess of $BaCl_2$ solution. The $BaSO_4$ is filtered off, washed, ignited, and weighed.

| Replicate No. | I. | II. |
|---|---|---|
| Wt. bottle plus sample | 15.4237 | 15.0125 |
| Wt. bottle minus sample | 15.0125 | 14.5805 |
| Wt. sample | .4112 | .4320 |
| Crucible No. | 1 | 2 |
| Wt. crucible—1st ignition | 13.3590 | 13.0073 |
| Wt. crucible—2nd ignition | 13.3588 | 13.0072 |
| Wt. crucible $BaSO_4$—1st ignition | 14.2953 | 13.9879 |
| Wt. crucible $BaSO_4$—2nd ignition | 14.2952 | 13.9877 |
| Wt. crucible | 13.3588 | 13.0072 |
| Wt. $BaSO_4$ | .9364 | .9805 |
| Per cent sulfur | 31.29 | 31.19 |
| Mean per cent sulfur | 31.24 | |

On the opposite left-hand page of the notebook should appear all the equations involved in the determination together with the calculations made. Any notes or precautions pertinent to the experiment, including mishaps which may have occurred such as the loss of sample or over-running of end points, should be noted. Also, incidental data such as rest points, balance swings, etc., may be recorded on this page.

**Significant Figures.** In quantitative work it is important to use the proper number of significant figures in recording and calculating analytical data. The use of more or less significant figures than are justified may create an erroneous impression as well as complicate the calculations involved.

A significant figure is considered to be a digit which denotes the amount of the quantity in the place in which it stands. Thus in the number 283, each digit is a significant figure. Zeros may be significant figures or may be used to locate the place of the decimal point. In the quantity 20.83, zero is a significant figure, whereas, in the quantity .083, zero is used to locate the decimal point and to indicate the order of magnitude represented by the other digits.

A general rule for recording analytical data is to retain as many significant figures as are necessary to make the last figure uncertain. In reading a burette calibrated to tenths of a milliliter, one can read accurately the tenths of a milliliter and estimate the hundredths of a milliliter. For example, in the quantity 35.46 ml., all the digits are retained as significant figures since only the last figure is uncertain.

The number of significant figures to retain in computations is very important. In general, when superfluous figures are dropped from a quantity, the last figure retained is increased by 1 if the following rejected figure is 5 or over. In adding or subtracting numbers, and in the sum or difference, retain in each number only as many figures to the right of the decimal point as there are in the least accurately known number. For example, in adding the following terms: $1.03 + 2.0567 + 3.023$, in which it is assumed that the last figure in each is uncertain, the sum is: $1.03 + 2.06 + 3.02 = 6.11$. In multiplying or dividing, retain as many significant figures in each quantity and in the result as are contained in the quantity having the least number of significant figures. For example, the product of the three quantities, $20.54 \times 0.0145 \times 2.5567$, in which it is assumed that the last figure in each is uncertain is: $20.5 \times 0.0145 \times 2.56 = 0.761$.

**Precision.** No analytical method is entirely free from possible error and the precision of the method is directly related to the amount of reduction of that possible error. The magnitude of the error involved in the different quantitative methods is dependent upon several factors. The analyst should consider these factors in order to minimize their effect whenever possible and also to ascertain the value which may be placed upon the results obtained. These factors include:

1. *Personal factors*—varying with the individual and depending upon his skill, training, and experience. The same precision cannot be expected from experienced and inexperienced analysts.
2. *Instrumental factors*—varying with the construction and precision of the instrument as well as its condition. These factors may be minimized by selecting the proper instrument, checking, and calibrating it before use. The calibration of balance weights and volumetric apparatus should be stressed.
3. *Methods employed*—all methods are subject to certain characteristic errors. Of these, errors involved in sampling, manipulation (weighing, precipitating, transferring, filtering, washing, igniting, titrating, etc.), and calculation, may be reduced to a minimum by the careful analyst. Appreciable errors, however, may originate in a method because the reactions involved do not go to completion but reach an equilibrium. These errors are inherent in the method and represent a constant anticipated error when using that method.
4. *Quantity of constituent analyzed for*—as a rule, the smaller the amount of constituent, the greater the error involved and the less the anticipated accuracy.

All analytical determinations are made in duplicate and, in general, it is assumed that if the results check each other closely, they are correct. While this is usually true, it happens occasionally that although duplicate results may agree closely they may be incorrect, since check results are dependent to a large extent upon identical conditions in the two analyses and, thus, the same error may have occurred in both cases. However, if the duplicate results fail to check each other, it is a good indication that neither result in itself can be considered dependable and a repetition of the analysis is necessary. In the event two different methods were used and check results obtained, they are more likely to be correct than check results obtained by a single method.

*Retention or Rejection of a Result.* In making several replicate determinations on a sample, one of the results may be rather far removed from the average of the rest. Theoretically, this should raise a doubt as to the validity of any of the results since the presence of a disagreeing result would tend to indicate faulty technique. However, if the analyst has been very careful throughout the determination and has made no conscious error, for all practical purposes, the disagreeing result may be discarded if the following conditions are met:

1. A minimum of four independent determinations were made.
2. The average has been determined without including the questionable result.
3. After computing the deviation of each result from the average, the deviation of the questionable result is found to be at least four times the average deviation of the remaining results.

For example, suppose five independent determinations gave the following:

| | *Replicate Results* | *Deviation from Average* |
|---|---|---|
| | .1536 | 2 |
| | .1534 | 0 |
| | .1533 | 1 |
| | .1533 | 1 |
| | .1540 | 6 |
| Average (omitting the questionable result) | .1534 | 1.0 |

The result .1540 could be rejected since its deviation is six times the average deviation for the four other results.

*Calculation of Error.* The difference between the true value and the value found by analysis is the error of the particular determination. In working with unknown samples one does not know the true values for the samples. However, the true value may be approximated by calculating the mean value of a number of determinations. In the preceding example of recorded data on barium sulfate, the replicate determinations were found to be 31.29 and 31.19 per cent of sulfur. The mean value for the percentage of sulfur (31.24) is obtained by adding the values found for the replicates (31.29 + 31.19) and dividing this sum by the number of replicates (2).

The calculation of the percentage error of the determination is then based upon the mean value obtained. Using the preceding example of recorded data on barium sulfate, the deviations from the mean regardless of sign are .05 and .05. The mean of these deviations is .05 and the percentage error is $\frac{.05 \times 100}{31.24} = 0.16$. Although the percentage error allowed in various analyses will differ, in general, a 0.2 per cent error or less is striven for. In many types of analyses it is possible to obtain results with errors much less than 0.2 per cent, while in some analyses, errors of 1 per cent may be permissible.

Instead of expressing the precision or error as percentage error, it may also be expressed in parts per thousand. This latter term may be less confusing since analytical results themselves are usually expressed in per cent. Again using for an example the recorded data on barium sulfate, the two replicates differ from the mean value by .05 per cent and .05 per cent respectively. This means that the deviation of each in this case is .05 parts in 31.24 parts or 1.6 parts per 1000. An accuracy of one part per thousand is the best that can be anticipated for any method.

*Precision vs. Practicability.* The possibility exists that the analyst may attempt to be too accurate and so run into the danger of becoming impractical. It should be emphasized that the accuracy of the final result obtained is governed by the precision of the least accurate measurement involved. Thus, in a determination, if one of the measurements is accurate to one part per thousand, it is a waste of time and effort to make the other measurements involved more accurate than this. For example, in weighing a sample of less than a gram, it would have to be weighed to the nearest 0.1 mg. to obtain an accuracy of one part per thousand. If a sample larger than a gram were weighed, the same accuracy could be obtained by weighing to the nearest milligram. For practical purposes, the use of the final result should also be considered in conditioning the accuracy desired in the determination.

**Choice of Analytical Method.** Frequently several methods are available for a particular determination and from these the analyst must select one for his use. Several factors need to be considered in selecting the particular method. These involve speed, accuracy, and personal preference. For example, colorimetric methods are more rapid than gravimetric methods. For the analysis of minute quantities of material, colorimetric methods are as accurate or more so than gravimetric. However, for the analysis of a constituent present in large quantity, gravimetric methods are more accurate than the colorimetric. Forced with the necessity of selecting either a colorimetric or a gravimetric method, the analyst must base his decision on the amount of material being analyzed for, and whether accuracy or speed is of the greatest importance. Analytical techniques in certain methods are simpler and more readily mastered than others; consequently such methods will have a personal preference over the more difficult ones.

Whenever possible in this text, several methods are given for a particular determination so that the analyst or instructor will have the opportunity of choosing the method he prefers. The advantages and disadvantages of the methods are usually stated to help in making the selection.

**Utilization of Time.** The efficient analyst is unhurried in his work but utilizes all his time to the greatest advantage. The best time utilization is attained only when several analyses are proceeding at the same time. Obviously, it requires practically as much time to make one filtration or evaporation as a dozen.

After making a careful study of the work to be done, the efficient analyst devises a plan of procedure so that no time is wasted and the maximum amount of work is accomplished in the minimum amount of time. In order to follow such a plan of procedure properly, the equipment contained in the desk should always be scrupulously clean and ready to use. A further precaution to observe is that all beakers and other vessels used are properly labeled to prevent any mix-up.

**Care of Desk and Its Equipment.** Each student should feel a personal responsibility for the proper use and care of the laboratory desk and equipment. Good analytical results cannot be obtained with dirty and uncared for apparatus. Furthermore, a dirty and disorderly desk gives the impression that the analyst is careless and sloppy in his work. In many industrial plants, the analytical laboratory is the show place of the plant and all visitors are taken through it to impress upon them that the plant is chemically controlled. Hence, it is necessary that the analyst cultivate the habit of neatness, cleanliness, and orderliness in the care of his laboratory desk and its equipment.

**Clean Apparatus.** In most cases, apparatus may be cleaned by means of a brush with soap and water, followed by rinsing with distilled water and drying in a drying cabinet. When a more drastic cleaning is required or when the apparatus does not lend itself to a brush cleaning, a cleaning solution should be used. However, it should be emphasized that cleaning solution should not be used indiscriminately for general cleaning, but only when the cleaning cannot be accomplished by brush, soap, and water.

*Cleaning solution* may be prepared by adding 500 ml. of concentrated sulfuric acid to 75 ml. of a saturated sodium dichromate solution in an evaporating dish of sufficient size. After cooling, the solution should be stored in a glass-stoppered bottle.

Cleaning solution may be used repeatedly as long as it retains its reddish-brown color and is not too diluted. The active oxidizing agent in the solution is chromic acid, formed by the reaction of sulfuric acid on sodium dichromate. In the oxidation of organic matter, the active agent is destroyed and carbon dioxide, water, and chromic sulfate are formed.

$$H_2SO_4 + Na_2Cr_2O_7 + H_2O = 2\,H_2CrO_4 + Na_2SO_4,$$

$$3\,C + 4\,H_2CrO_4 + 6\,H_2SO_4 = 2\,Cr_2(SO_4)_3 + 3\,CO_2 + 10\,H_2O.$$

The positively charged chromium ion of chromic sulfate causes the solution to become green as the oxidizing ability of the solution is destroyed.

**Wash Bottle.** Every laboratory desk should contain one or two wash bottles of 500–1000 ml. capacity. The common type of wash bottle is diagramed in Fig. 1. To facilitate handling when used with hot water, the neck of the bottle may be insulated by wrapping with asbestos cord or other suitable material.

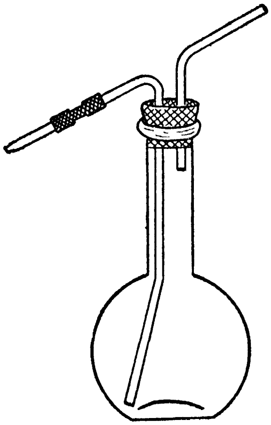

Fig. 1. Wash Bottle.

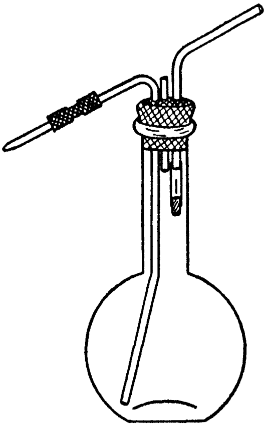

Fig. 2. Wash Bottle Equipped with Bunsen Valve.

Some analysts prefer a wash bottle equipped with a Bunsen valve, Fig. 2. The Bunsen valve permits one to cause a flow of water from the wash bottle by intermittent rather than constant blowing. This is especially helpful when using the wash bottle with hot water since the valve prevents steam from coming back into the mouth when one stops blowing. The Bunsen valve is prepared by cutting a slit in a piece of rubber tubing, plugging one end of the tubing with a short glass rod, and attaching the other end to the glass tube projecting through the stopper. The valve will open to allow blowing into the bottle, but when pressure is applied in the opposite direction, the edges of the slit in the tubing are forced together thereby sealing the opening.

**Marking Glass and Porcelain Ware.** Glassware is easily marked with a pencil on the sanded spots prepared for this purpose on the vessels, by gummed labels, or by means of a wax marking pencil. Porcelain ware is best marked with iron ink or marking compound, followed by ignition at a high temperature in an open flame. Porcelain crucibles may also be marked by filing small notches around the rim of the crucible.

**Use and Care of a Desiccator.** The main function of a desiccator is to provide an atmosphere in which the aqueous vapor tension is practically zero. This is accomplished by placing an efficient desiccating agent within the desiccator, usually in the bottom. The Hempel [1] desiccator holds the desiccating agent in a rim around its cover. Although this type of desiccator is more efficient than the common type, it is not used extensively because of the danger of spilling the desiccant upon the material to be kept dry.

Various types of desiccants are in common usage and the choice of a suitable one is largely a matter of personal preference. Anhydrous calcium chloride, barium oxide, and concentrated sulfuric acid are, perhaps, the most common desiccants. When sulfuric acid is used, the bottom of the desiccator is usually filled with pieces of broken glass or short pieces of glass tubing, and the sulfuric acid added to almost the top of the layer of broken glass. In this way the danger of spilling or slopping the desiccant when moving the desiccator is eliminated.

All desiccants deteriorate with use through the absorption of water vapor and so from time to time must be replaced by fresh desiccant. When the age and usage of the desiccant in a desiccator are not known, it is always a good policy to clean and refill the desiccator with fresh desiccant.

To retain the efficiency of the desiccator, it is necessary to insure a minimum amount of water vapor to come into contact with the desiccant. The desiccator lid should be thoroughly greased with vaseline so that an air-tight seal is maintained. Also, care should

[1] Hempel, *Ber.*, **23**, 3566 (1890).

be exercised that no *wet* dishes or *wet* substances are ever placed in the desiccator. In using the desiccator, the cover should only be removed for the minimum time necessary to effect the introduction or removal of the dishes from the desiccator. This will insure the minimum amount of laboratory air, usually fairly well saturated with water, to come into contact with the desiccant. The difficulty in following this procedure closely is that the introduction of hot dishes will cause an expansion of air within the desiccator to the point of blowing the lid off. In this case, the analyst should hold the lid on in the plain type of desiccator (Fig. 3), but as the pressure increases slide the lid off slightly one or two times to permit some of the heated air to escape and so reduce the pressure. A vacuum desiccator (Fig. 4) is preferable to the plain in this situation since the pressure may be released quickly and easily by opening the stopcock on the desiccator lid for a brief interval.

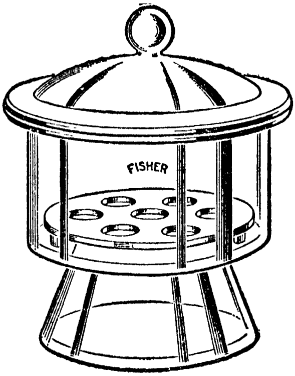

FIG. 3. Desiccator. (Courtesy of Fisher Scientific Co.)

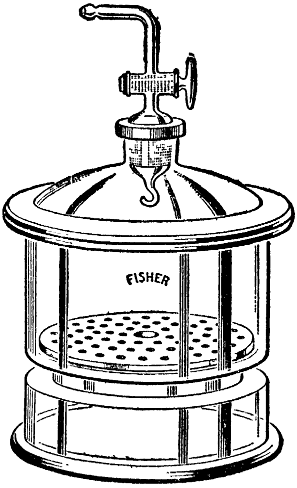

FIG. 4. Vacuum Desiccator. (Courtesy of Fisher Scientific Co.)

In carrying the desiccator around the laboratory, the rim should be held tightly with both hands to prevent the cover from slipping off and breaking. Care should also be taken so that the vessels within the desiccator do not upset. The plate in the desiccator should contain holes of the proper size so that crucibles may be seated in them. With proper care and usage, a desiccator should retain its maximum efficiency throughout the semester.

**Use and Care of Platinum Ware.** Platinum ware is expensive and should be handled accordingly. It is cleaned by rubbing with moist sea-sand, being careful not to bend the crucibles or dishes as they are usually of lightweight construction and are easily deformed. Boiling platinum ware in a hydrochloric acid solution (1:1) is also resorted to as a method of cleaning. If this is not sufficiently drastic, fuse with potassium acid sulfate ($KHSO_4$) and dissolve the fused mass with hot water. Obviously, *aqua regia should never be used* to clean platinum ware. In general, platinum ware should be cleaned with the least loss or injury, immediately after each time it is used.

Care must be exercised in heating platinum ware so that the reducing flame of the burner does not come into contact with the ware, as unburned carbon forms platinic carbide, causing the platinum ware to become brittle. In general, platinum ware, when heated, should not be permitted to come into contact with other metals. Hot platinum crucibles or dishes are always handled with a platinum or heavily nickel-tipped crucible tongs and are supported when heated on triangles of platinum, clay, quartz or chrome-nickel alloys.

Although platinum is quite resistant to acids and is not oxidized in the air, it is attacked by a number of substances at ignition temperatures. For example, platinum is attacked by solutions containing free chlorine, bromine, iodine or ferric chloride. At a red-heat the caustic alkalies, alkaline earths, nitrates and cyanides, barium and lithium hydrates also attack platinum. Compounds of lead, silver, tin, bismuth, arsenic, and antimony should not be ignited in platinum ware since the reduction of metals having low melting points may result in the formation of alloys with platinum which destroys its usefulness. Fusions of any of these compounds should not be made in platinum ware. Care must be exercised when igniting phosphates in platinum ware as the presence of reducing substances, such as carbon from burning filter paper, may cause the reduction of small quantities of phosphorus; which, if it combines with platinum, causes the platinum to become brittle. In general, do not heat unknown substances in platinum ware.

**General Laboratory Reagents.** Solid and liquid chemicals may be purchased with varying degrees of purity. The analyst should be familiar with the various grades of chemicals and the conditions under which each may be used. In the interests of economy, he should consider whether the purest grade, highest priced, chemical is required in a particular method or whether a lower grade, cheaper priced, chemical might be used as well. He should also consider whether the impurities in a reagent chemical might affect the results of the analysis and, if so, the importance of this effect and how it could be nullified by running a blank, etc.

Reagent chemicals may be classed as follows:

*C.P. and Analyzed C.P. Grades.* C.P. (chemically pure) reagents are comparatively high grade reagents. However, since there are no definite specifications relative to the grade, certain of the manufacturers have produced "analyzed" chemicals for reagent use. These analyzed chemicals carry a label giving the complete analysis of the product and indicating if they meet the specifications published by the "Committee on Analytical Reagent Chemicals" of the American Chemical Society.[1]

*Reagent Grade.* High grade chemicals conforming to definite specifications established by the manufacturer and usually meeting the specifications of the American Chemical Society.

*U.S.P. Grade.* These chemicals meet the requirements of the United States Pharmacopœia. Such chemicals are sufficiently pure for many reagent purposes.

*N.F. Grade.* Chemicals which meet the requirements of the National Formulary.

*Purified Grade.* Used as a grade designation for a chemical where a U.S.P. or N.F. standard does not exist.

*Technical or Commercial Grade.* Not a highly purified product and seldom used for the preparation of analytical reagents.

While in a general way the labels on the bottles may be depended upon for purity, it is unwise to trust them implicitly. Not only may mistakes occur in the packaging of the product but, if it has been opened several times, moisture and other impurities may have contaminated it. The careful analyst should be familiar with the methods of testing the purity of the chemicals and the elimination of the effect of the impurity by means of a blank determination. The "Committee on Analytical Reagent Chemicals" of the American Chemical Society has published, in addition to specifications, tests for the determination of the impurities present in the more commonly used reagent chemicals.[1]

**Use and Care of General Laboratory Reagents.** A good motto for every quantitative analyst would be, "Take nothing for granted." Unfortunately, in a large class, a few things must be taken for granted. For example, it must be assumed that the reagents used in a determination have the correct concentration indicated on their labels and that they are not contaminated. This assumption will be correct *only* if each individual is extremely careful in the use of these reagents common to all. Certain precautions necessary to accomplish this are:

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[1] *Ind. Eng. Chem.*, **17**, **756** (**1925**); **18**, **636**, **759** (**1926**); **19**, **645**, **1369** (**1927**); **20**, **979** (**1928**). *Ind. Eng. Chem., Anal. Ed.*, **1**, **171** (**1929**); **2**, **351** (**1930**); **3**, **221** (**1931**); **4**, **154**, **347** (**1932**); **5**, **289** (**1933**); **12**, **631** (**1940**).

1. Never remove a stopper from a bottle without insuring that the stopper is replaced on the bottle from which it was taken. Stoppers should not be laid on desks, etc., as they collect impurities in this way which are then later transferred to the contents of the bottle.
2. Never remove a solution from the reagent bottle with a pipette and so avoid contaminating the solution with impurities from wet or dirty pipettes. Pour the solution into a clean dry beaker and measure out the required amount from this, discarding the excess remaining in the beaker. (Do not pour any of the excess solution back into the reagent bottle in the interests of economy.) Obviously, only remove as much of the solution from the reagent bottle as will be required.

# PART II

# GRAVIMETRIC ANALYSIS

## CHAPTER II

## OPERATIONS OF GRAVIMETRIC ANALYSIS

### SAMPLING[1]

Very rarely does the analyst receive samples in a form ready for analysis. He is usually required to obtain a sample which is representative of the whole from a can of milk, a tub of butter, a carload of wheat, a bag of fertilizer, an acre of soil, etc. Securing such a sample is one of the analyst's most difficult problems, since the value of his analytical results depends greatly upon securing a representative sample.

**Considerations Involved in Obtaining a Representative Sample.** In obtaining a sample for analysis, the analyst attempts to secure the smallest sized sample which will be truly representative of the whole mass involved. Since the nature and quantity of the materials that may be submitted to the analyst vary so greatly, no definite procedures can be stated for the securing of an adequate sample. There are certain factors, however, which serve to guide the analyst in securing an adequate sample. These are homogeneity of the material, accuracy of the methods of analysis, use to which the results are put, the cost involved, and the quantity of material to be sampled.

If the sample is homogeneous, a small sample may be secured at random. As the degree of heterogeneity increases, the care required in securing the sample must correspondingly increase in order that the sample be representative of the whole. If the methods of analysis are very accurate and minute differences in results are significant, great care must be exercised in securing a true sample. On the other hand, if the results are to be used only to determine whether the values fall within a certain range, less care may be taken in obtaining the sample. The cost of preparing a sample for analysis is an important item, and an attempt is always made to secure the smallest sized sample possible.

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[1] Although discussed only under gravimetric analysis, it should be emphasized that sampling techniques are equally important in volumetric and other types of analyses.

The amount of material from which the sample is to be obtained may vary from that present in a small container to a trainload of the material or an acre of soil. Small containers present no problem in sampling since the contents of the entire container may be taken as a sample. Larger amounts of material require the removal of small samples from different portions of the material, the mixing of these samples into a composite and the removal of a sample representative of the whole. This procedure involves the use of instruments to remove samples from different depths of the material so that an entire cross section of the material is represented in the sample. A further consideration is the number of such individual samples to take from a given lot of material for the composite sample. This composite of small samples may make quite a sizable sample and must necessarily be reduced to a size suitable for analysis. This is usually accomplished by a series of standard manipulations involving mixing, quartering, and possibly grinding.

**Samplers.** Several instruments, or samplers, are used for the proper sampling of various materials. Of these, the most important are the "thief" used in sampling liquids, the "trier" or "sampling tube" to obtain a cross-section sample from dry material, the "auger" or "drill" to remove samples from solid material into which a trier cannot be inserted, and the "pelican" to abstract samples from a continuous flow of material.

The thief is essentially a tube 24–36 in. long with an opening or openings for the liquid to flow into it when inserted into a drum, tank, or other container of liquid. The opening or openings can then be closed and the thief containing the sample removed from the container. Modifications of this instrument permit sampling a liquid at any depth or throughout its entire depth.

Several triers or probes of different design and size are available. In general, they consist of a tube varying from 12 to 60 in. in length. At the top of the tube is a handle by which the instrument is forced into the material and later withdrawn. In one type, the handle is also used to open and close the slot through which the sample enters the tube. The simplest type has the tube open at the bottom, so that when the trier is inserted, the material in the path of the trier is forced into the open end and thereby removed as a sample. Most of the triers are closed at the bottom end which is then tapered to a point to facilitate the insertion of the trier into the product. These triers have slotted openings extending the length of the tube. The opening should be large enough for the largest particles of the product to pass into the tube without segregation of material. When used, the trier should be inserted with the slot down, turned, allowed to fill and then withdrawn. With slight modifications (wider slot and sharpened edges) this type of trier can be used to sample butter and similar products. A double-tube trier, Fig. 5, is used for removing grain samples from various levels in carload lots.

The auger or drill is used to remove a sample core from solid material which cannot be sampled by a trier. Soil samples may be obtained from any desired depth in this way. Frozen products, such as eggs, etc., may be sampled readily by this procedure.

The pelican is used primarily in the sampling of a falling stream of grain, for example, while grain is being spouted into a ship's hold. The pelican is nothing more than a scoop attached to a long handle, Fig. 6. As the grain falls from the end of the spout to drop into the ship's hold, the pelican is thrust through the grain stream at definite intervals, thereby obtaining a cross-section sample of the grain stream. The composite of these samples obtained must then be reduced to laboratory sample size.

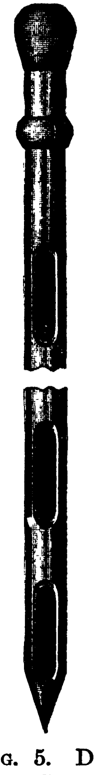

FIG. 5. Double Tube Sampler. (Courtesy of Burrell Technical Supply Co.)

**Number of Portions for Composite Sample.** An extremely important point in sampling is the number of individual samples which should be taken from a lot so that the composite sample will be representative of the entire lot. This is especially true in sampling large lots of material. For example, in sampling a carload of grain, five or more individual samples are removed by a trier from predetermined distributed locations in the car. In an A.O.A.C. committee report on sampling feedstuffs,[1] the established sampling technique for fertilizers [2] was suggested as acceptable also for feedstuffs. In sampling large lots of bagged material, this involved removing sample cores from not less than 10 per cent of the bags present unless the process required removing cores from more than 20 bags, in which instance, a sample core was taken from 1 bag for each additional ton represented. If the lot to be sampled is less than 100 bags, sample at least 10 bags, and if less than 10 bags, sample each one.

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[1] Jeffers, *J. Assoc. Off. Agr. Chem.*, 25, 854 (1942).

[2] *Assoc. Off. Agr. Chem.*, "Methods of Analysis" (1940), p. 20.

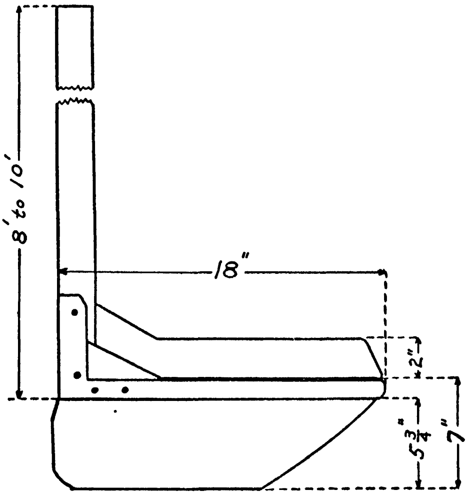

Fig. 6. Pelican.

Jacobs[3] gives the following suggestions for sampling foods:

> In the case of single packages or a small batch, if it be convenient, the entire package or batch should constitute the sample. For moderately larger batches or lots, from 10 to 20 per cent of the number of packages comprising the batch or from 5 to 10 per cent of the weight of the food material should be sampled and sufficient should be taken to yield from 1 to 2 pounds of sample. For very large lots such as case lots, bag lots, churn lots, etc., a general rule to follow is to sample a number of containers equivalent to the square root of the number in the lot. If experience has shown that no composite sample can be made, the food taken from each container should be analyzed separately.

**Reduction of Composite Samples to Laboratory Sample Size.** The reduction of large composite samples to a size suitable for analysis in the laboratory involves several manipulations including mixing, quartering, and possibly grinding.

Mixing of dry, finely divided, solid material is accomplished by placing the composite sample in the center of a large sheet of paper or oilcloth. Then by rolling the sample diagonally across the paper or cloth and alternating the direction of rolling, in directions 1, 2, 3 and 4, in order (Fig. 7), the sample is thoroughly mixed. The only necessary precaution to observe is that the corner of the paper, when drawn across, must be held low down so that the pile of material is turned over rather than caused to slide. By turning over, the material is mixed without segregation of the larger and smaller particles.

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[3] Jacobs, "Chemical Analysis of Foods and Food Products," D. Van Nostrand Co., Inc. (1938), p. 8.

When the material has been mixed sufficiently, the pile is made approximately circular and divided into quarters. Two opposite quarters are saved and the other two discarded. These two quarters are again mixed and quartered, and the process repeated, until a sample small enough for analysis is obtained. Instead of mixing and quartering as described, a divider or riffle may be used, making possible a more rapid mixing and dividing of the sample.

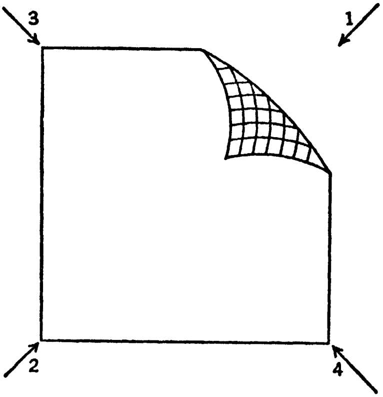

Fig. 7. Diagram Illustrating Method of Mixing Dry and Finely Divided Solid Material.

**Grinding to Correct Particle Size.** In the event that the material is in such a large state of subdivision that it cannot be properly mixed and quartered, it must first be ground to a state of fineness so that it can be mixed thoroughly. The material must finally be in such a state of subdivision that the chance removal of any particle will not affect the analysis of the remainder. Obviously, the nature of the material will determine the size of particle permitted. Agricultural products are usually ground to pass through sieves having circular openings 0.5 to 1.0 mm. in diameter. Dry materials should be ground finer than is necessary to pass a 1-mm. sieve in order to prevent particle segregation. Good results are obtained if the material is ground to pass a 35-mesh sieve. In grinding a material to a definite particle size it is essential that the entire material be ground to pass through the sieve and that none be discarded. Frequently, certain structures in agricultural products are ground with difficulty but they must be included in the sample in order to give a true picture of the whole. The grinding or disintegration of the sample may be accomplished by any one of several means depending upon the product. There are available for this purpose various types of grinding mills—Wiley mill, ball mill, mortar and pestle, mechanical high-speed beaters or blendors, and meat grinders.

Pulpy materials such as fruit and vegetable products, frozen desserts containing nuts and fruits, and meats may be disintegrated and converted into a homogeneous sample by means of mechanical mixers. Several such mixers, similar in type to a high-speed malted milk mixer, or mechanical beater, so-called blendor, are on the market.

**Sample Storage.** The samples prepared for analysis should be stored in sealed containers to prevent moisture changes. Samples subject to spoilage may require refrigeration or the addition of a preservative. After analysis, the remainder of the sample should be retained in the event a dispute arises relative to the results obtained. This latter point is very important in the analysis of substances for adulteration or for meeting certain specifications, since lawsuits may be involved and a further analysis of the product required.

**Mixing and Sampling Liquids.** Liquids may be mixed easily by stirring, shaking, or pouring from one container to another. If samples are removed immediately after cessation of mixing, they will be representative of the whole. For sampling large batches of liquids, a "thief" may be used.

## SOLUTION AND EVAPORATION

Samples that are water soluble are normally dissolved in water. In some instances an acid medium is necessary to effect solution. Usually dilute nitric or dilute hydrochloric acid is used for this purpose. In the event that a basic medium is required, a sodium hydroxide solution is frequently used. The volume of solvent should always be kept to a minimum, usually not over 100 ml., since the larger the quantity of solvent and wash water required, the more precipitate is liable to be lost later.

At times, samples will not go into solution in an acidic or basic medium but require a fusion to get them into a soluble form. The most common fluxes are sodium carbonate or potassium acid sulfate for materials of an acidic or basic nature, respectively.

It is advisable to keep solutions covered as much as possible to protect them from contamination. Frequently, it is necessary to evaporate solutions over a flame or on the steam bath, in which case the vessel may be covered or uncovered. If it is covered, some device, such as glass hooks hung over the side of the vessel, should be used to raise the cover glass slightly off the beaker.

The main difficulty experienced in the evaporation of solutions is caused by superheating at the bottom of the vessel through incomplete diffusion of the heat. As a result, a comparatively large amount of steam is given off at a time, causing a violent eruption of the solution with the possibility of loss of solution through spattering. To eliminate this difficulty, some means of preventing superheating is necessary. The addition to the solution of glass beads, pieces of porous plate or pumice stone causes the steam to be given off gradually, and thus prevents superheating. Stirring the solution mechanically or bubbling a stream of air through the solution is also an effective means of overcoming this difficulty.

## PRECIPITATION

Precipitation is used to convert the constituent which is being determined into a form that is easily separated from the solution or to remove from solution some constituent which will cause trouble in a subsequent procedure. It is necessary, therefore, to consider the factors involved in the procedure of precipitation.

In order that the constituent be precipitated completely, it is necessary that the reaction involved proceeds to completion. While theoretically all reactions are reversible, only those reactions which for all practical purposes are complete, may be used as a basis for quantitative analysis.

A second consideration is to secure as complete a separation of the precipitate from the solution as it is possible to obtain. To accomplish this, the precipitate should be practically insoluble in the solution and be made up of large crystal particles. Consequently, the constituent is precipitated in its most insoluble form and the conditions of the experiment so adjusted that the precipitate remains insoluble.

The particle size of the precipitate is very important in that large grainy crystalline precipitates are more easily and effectively separated from the solution. Small particles, colloidal in nature, may be able to pass through the filter and be lost. Small crystals also have a larger surface area for the adsorption of impurities than do the large crystals. Furthermore, large particles can easily be washed free from impurities, whereas small colloidal-like particles plug up the pores of the filter and require a long and difficult washing procedure.

Several factors are involved in securing large crystalline particles. The addition of the precipitating agent slowly, by drops, favors the production of large crystals; so also does heating the solution during and for a period of time after the precipitation. This causes the small crystals, which are more readily soluble than the large ones, to dissolve and reprecipitate on the larger ones. In this way the larger crystals grow at the expense of the smaller ones.

Enough of the precipitating agent is added to insure complete precipitation, but a large excess is avoided. It is customary to calculate the amount of precipitating agent necessary for complete precipitation, and then to add a slight excess. To insure that precipitation is complete, the supernatant liquid or a small portion of the filtrate may be tested with the precipitating agent to determine if further precipitation occurs.

Within limits, precipitates are less soluble in a solution containing a common ion than they are in water. For example, barium sulfate is more insoluble in a solution of barium chloride than in water; hence an excess of barium chloride is added in the precipitation of barium sulfate not only to insure complete precipitation but also for common-ion effect. However, the presence of an excessive quantity of common ion in a solution will cause a greater solubility of the precipitate and must be guarded against.

Sometimes when precipitates are formed they occlude, or mechanically carry down, other substances in the solution. These substances may practically be surrounded by the crystal structure and consequently cannot be washed from the precipitate, even though they are completely soluble in water. To eliminate the danger of occlusion, the precipitating agent is run into the solution slowly, with constant stirring, so that the crystal structures are formed slowly and entirely free from other substances.

Impurities may be adsorbed on the surfaces of the crystalline precipitate. These are usually quite readily washed off. A further difficulty may occur through the precipitation of varying quantities of an impurity as an insoluble precipitate. In this instance, the entire precipitate is dissolved and reprecipitated under conditions which will prevent the precipitation of the impurity.

## FILTRATION

The object of filtration is to separate the precipitate or suspended matter from a liquid. This may be accomplished by pouring the material upon a filter paper suspended in a funnel. The paper permits liquid to pass through its pores but retains the solid precipitate.

Great care is required in transferring the material from a beaker to a filter paper so that none of the material is spilled or lost. The stirring rod is used to direct the liquid from the tilted beaker into the filter. The stirring rod, equipped with a rubber policeman, is also used to dislodge and scrub the precipitate from the surfaces of the beaker into suspension in the water. The last particles of precipitate may be washed from the beaker into the filter by a stream of water directed from a wash bottle, while the beaker and stirring rod are held in the proper position.

The filter paper should fit the funnel properly in order to insure rapid filtration. This is accomplished by folding the filter paper in half, then into quarters of slightly unequal size. The corner torn off the smaller quarter will permit a better fit at the top of the filter (see Fig. 8). Using the larger quarter, fit the filter into the funnel and moisten with water to hold the filter in place. If the filter has been properly folded and fitted into the funnel, the top of the filter should fit tightly around the funnel, whereas the bottom of the filter should be free from the funnel. This situation permits rapid filtration.

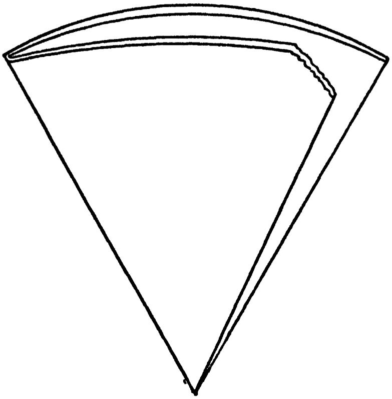

FIG. 8. Filter Paper Folded to Fit Tightly in a Funnel.

Quantitative work requires a special grade of filter paper which has been previously treated so that it is practically ash-free upon ignition. The size of the filter is, of course, governed to a large extent by the amount of precipitate. Since the larger the filter, the more wash water will be required and the more danger there is in loss of precipitate, the filter is always kept as small as possible. The particle size of the precipitate is important in choosing a filter paper of proper pore size. Very fine precipitates require slow filters with very fine pores, while in the case of larger particles, a more rapid filtration is possible through the use of filter paper with larger pores. Quantitative filter paper is considerably more expensive than other grades of filter paper and should only be used when a quantitative filtration is required.

The speed of filtration may be increased materially by reducing the pressure on one side of the filter. In this case, Gooch crucibles employing asbestos mats are the more common filtering means. Due to the ease of tearing, ordinary filter paper does not function well under conditions of reduced pressure, although a special "hardened" filter paper will work satisfactorily. Porous alundum crucibles, or crucibles equipped with porous fritted glass bottoms, may also be used.

In the preparation of a Gooch crucible for filtration purposes, a medium length, acid and alkali washed and ignited, asbestos fiber is preferable. The absestos is suspended in water and poured into a Gooch crucible placed on a suction flask. Allowing the fiber to settle in the Gooch crucible without the use of suction permits the larger and heavier fibers to settle out first upon the pores of the crucible and so prevents the plugging up of the pores by the finer fibers. After a minute's rest, suction is applied to the crucible and more suspended asbestos may be added to give an asbestos mat of approximately 1/16th to 1/18th inch in thickness in the bottom of the crucible.

Using suction, the asbestos mat is then washed thoroughly with approximately 500 ml. of water, passed through in quantities of 10–20 ml. at a time, permitting the crucible to drain completely between each addition. This washes out any soluble matter from the mat and also thoroughly packs the mat so that it will function properly when in use.

After the crucible has been thoroughly washed it is usually dried in a 100° C. moisture oven. The drying process may be shortened somewhat if the wet crucible is first washed with alcohol to remove the water, then with ether to remove the alcohol, and then dried.

Another means of speeding up filtration is to filter solutions when hot. Water at 100° C. has only one-sixth the viscosity of water at 0° C., and since the rate of flow of a liquid through a filter is dependent largely upon viscosity, the advantage of using a hot solution is obvious.

## WASHING

Washing the precipitate is necessary to remove all soluble impurities from the precipitate so that it is of a definite chemical composition. In general, the impurities are soluble salts and are easily removed by washing. If there is an excessive amount of impurity present, it may be necessary to redissolve the precipitate and to reprecipitate it. In this second precipitation, the amount of impurity present is small in comparison with the amount of precipitate and can be removed easily.

Washing the precipitate by decantation is practiced whenever possible. This permits a more thorough washing of the precipitate free from impurities in the containing vessel with a minimum quantity of wash water. As has been previously mentioned, all precipitates are soluble to a slight extent; consequently the amount of wash water employed should always be kept to the minimum which will remove all soluble impurities.

To insure the maximum washing with the minimum amount of wash water it is preferable to wash with a number of small portions of water, permitting each portion to drain from the precipitate before making the next addition. For example, if 150 ml. of wash water were to be used, ten washings with 15 ml. portions would be 23 times as efficient as six washings with 25 ml. portions.

The use of hot water will tend to facilitate the washing as well as filtration of precipitates, in that substances are usually more soluble in hot water than in cold. Care must be taken that the upper edges of the filter are thoroughly washed with each addition of water since soluble salts may be held quite tightly by the filter.

To determine the completion of the washing procedure, the washings are usually tested for some specific impurity, and when this is no longer present, it is assumed that the precipitate has been washed free from all impurities. For example, in the sulfate determination, where a barium chloride solution is used for the precipitation of barium sulfate, the precipitate is washed until the washings give no test for the chloride ion. Since the chloride ion is present in greater quantity than any other impurity at the time of precipitation, it is reasonable to assume that, if the precipitate is washed free from chloride ion, it should also be free from all other impurities.

## DRYING AND IGNITION OF PRECIPITATES

After the precipitate has been filtered off and washed, the filter paper is removed from the funnel, folded several times, and placed in a previously heated and weighed crucible. If time permits, the crucible and contents are dried in a 100°–110° C. oven for several hours or over night. A more rapid drying of the precipitate is accomplished by intermittent heating of the crucible and contents with a burner, alternately applying and withdrawing the flame until the filter is dry.

The dry precipitate is then ready for ignition. If the burning filter paper has no effect upon the precipitate, the crucible and its contents are heated with free access to air until all carbonaceous matter is destroyed. Care must be taken, however, to burn the filter paper slowly as violent burning is likely to cause a mechanical loss of ash in the air currents produced.

In some cases the burning filter paper effects a reduction or otherwise influences the composition of the precipitate. It is then necessary to free as much of the precipitate as possible from the paper and ignite the paper first. After most of the carbon in the paper has been destroyed, the bulk of the precipitate is added, and the ignition carried to completion.

The ignition of precipitates may effectively be carried out over a gas burner. A certain amount of supervision is required to regulate the temperature while ashing and there is also the possibility of carbon deposition on the crucible during the ignition. A thermostatically controlled muffle furnace, adjusted to the proper ignition temperature, is preferable for the ignition of precipitates and the ashing of agricultural and biological materials.

When using a muffle furnace adjusted to a constant ignition temperature, it is necessary to ignite previously the precipitate or material over a burner to get rid of most of the carbonaceous matter. This will prevent the too rapid combusion of the organic matter in the hot furnace and thereby eliminate the danger of mechanical loss of inorganic matter.

## CRUCIBLES

Porcelain crucibles are generally used for the ignition of precipitates and also for the ashing of agricultural materials. Certain disadvantages in using them are that they are easily broken, do not conduct heat as readily as the metal crucibles, and are liable to be affected by certain reagents. In the latter event, platinum crucibles or crucibles of various metallic alloys must be used. The advantages of porcelain crucibles reside in their low cost, resistance to the reducing gases of burners, and resistance to many substances to which platinum is sensitive.

Since analytical determinations are usually made in replicate, it is essential that the porcelain crucibles be marked. This can best be accomplished by numbering the crucible with an iron ink or special marking fluid. After the ink or fluid has dried, the crucible is heated gently at first and finally to a white heat in a flame. Obviously, the marking must be made before the crucible has been ignited and weighed since there will be a change in weight due to the marking.

When it is necessary to ignite porcelain Gooch crucibles, they are placed into ordinary procelain crucibles and heated over a flame. This eliminates deposition of carbon on the Gooch crucibles and also prevents the flame from striking the asbestos mat.

After ignition of the crucibles alone, or when containing precipitates, they must be cooled to room temperature before weighing. To prevent absorption of moisture, the crucibles must be cooled in a moisture-free atmosphere in a desiccator. The preparation and proper use of a desiccator are important factors in securing good analytical results (see p. 10).

## CHAPTER III

# THE ANALYTICAL BALANCE, WEIGHTS AND WEIGHING

### THE ANALYTICAL BALANCE

Quantitative analysis had its origin when the analytical balance became a part of the chemical laboratory. It is the most important tool of the analytical chemist and, as such, should be understood and appreciated properly. Thus, it is essential to consider briefly the construction of the balance and the proper method of using it.

The lever principle is the basis for the construction of the analytical balance. The beam, or lever, has attached to its center an agate knife-edge which rests upon an agate plate, making a practically frictionless fulcrum. A pan is suspended from each end of the beam by means of a stirrup which rests on a bearing similar to the knife-edge plate support of the beam. The pans rest upon pan arrests which may be lowered by means of a knurled screw, the pan release, permitting the pans to swing freely. Another knurled screw at the front of the balance, the beam release, effects the raising of the knife-edge of the beam off the agate plate when the balance is not in use. The working parts of the balance are protected from dust and air currents while in operation by enclosure within a glass case, with a glass section in the front which may be raised and lowered while operating the balance. The principal features of the balance are illustrated in Fig. 9.

The construction of the balance is largely responsible for its accuracy and sensitiveness to slight differences in load. The beam should be as light as possible, yet with sufficient rigidity so that it does not bend. The longer the beam, the greater will be the sensitivity of the balance. However, the limiting factor here is length of beam with sufficient rigidity and without too much weight. The central knife-edge and the end knife-edges must be in a state of stable equilibrium. This is accomplished by having the center of gravity lie slightly below the central knife-edge. The arms of the balance should oscillate fairly rapidly, although this is determined somewhat by the sensitivity required, since the sensitivity increases with the time of oscillation. The sensitivity of the

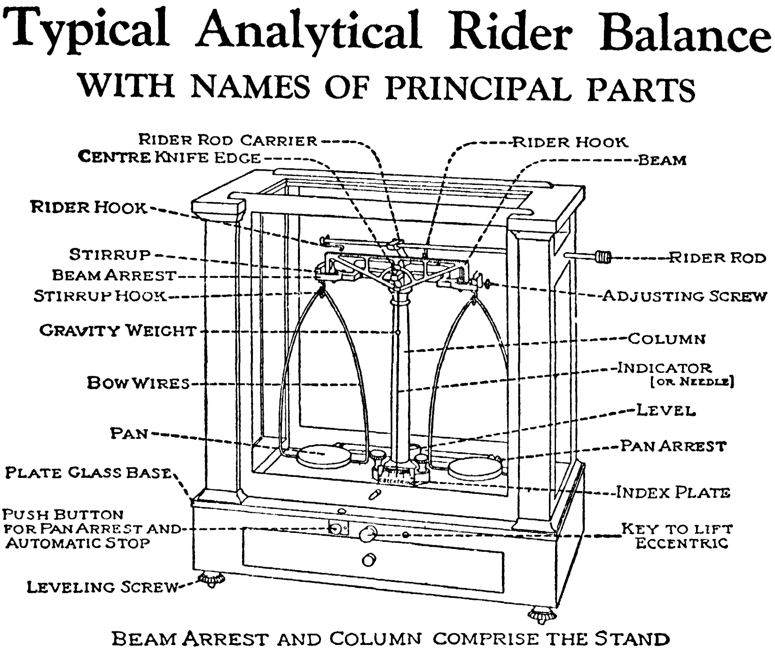

FIG. 9. Analytical Balance. (Courtesy of Christian Becker.)

balance should be such that a load of 1 mg. on the beam will deflect the pointer 3 to 4 divisions on the scale.

**Balance Features.** Balances vary in capacity, sensitivity, and the rapidity with which a weighing may be made. In purchasing or selecting a balance for use in the laboratory, the analyst should consider these features in order that the most efficient balance is obtained.

*Capacity* of ordinary student balances is usually 150–200 grams. When a greater sensitivity is required, as in microchemical and assay balances, the balance may have a capacity of 25 or even 5 grams. For calibrating volumetric flasks, etc., balances with a capacity up to 1000 grams are required.

*Sensitivity* of the balance varies with the length of beam, the weight of the beam, the speed of oscillation, and the condition of the knife-edges. In general, the longer the beam the slower the oscillation and the greater the sensitivity. However, the smaller the weight of the beam, the greater the sensitivity. This fact will condition the length of the beam since increasing the length will also increase the weight. Balances with a 7-in. beam and a sensi-

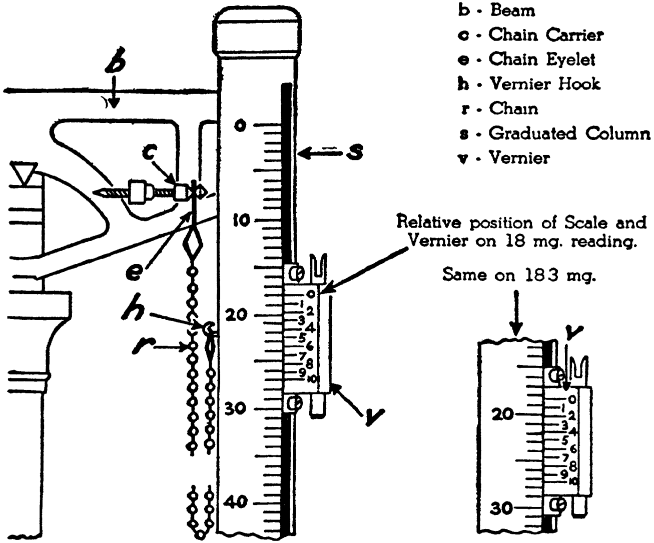

FIG. 10a. View of Portion of Balance Showing Graduated Column and Vernier and Method of Attachment of Chain. (Courtesy of Christian Becker.)

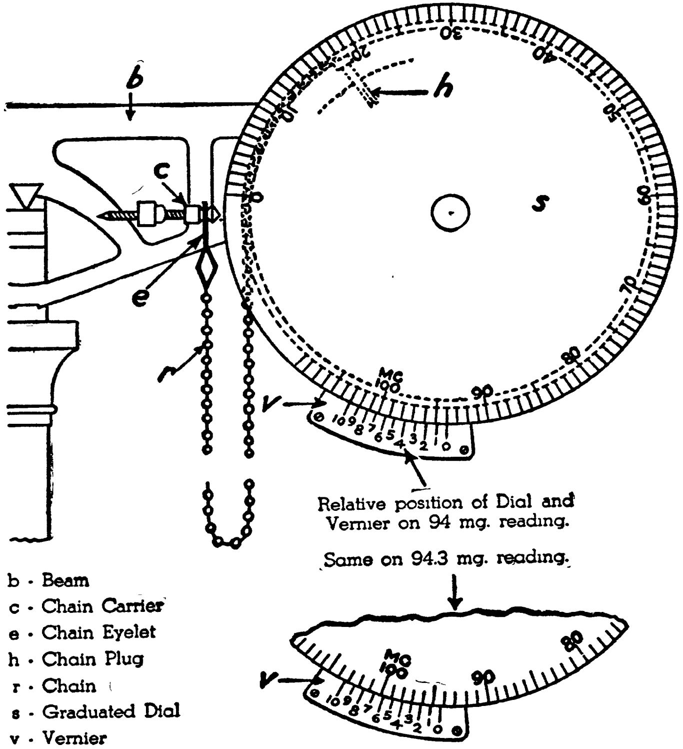

FIG. 10b. Dial Type Chainomatic Balance. (Courtesy of Christian Becker.)

tivity to one-twentieth milligram will make a complete oscillation in 12–14 sec. Increasing the speed of oscillation by adjustment on the pointer will increase the speed of weighing but tend to decrease the sensitivity. Dulled knife-edges and chipped or worn plates acquired through hard usage decrease the sensitivity of the balance.

*The chain rider* (illustrated in Figs. 10a and 10b) facilitates rapid weighing. A balance equipped with a chain rider (chainomatic balance) has the same construction as the ordinary balance except that the beam weighs the tenths of a gram. Weighings obtained between 0.1000 and 0.0001 gram are obtained from weight added to the beam by the length of an attached uniform chain, whose length supported by the beam may be changed by rotating a crank on the right side of the balance case. This type of balance eliminates the use of any fractional balance weights. Furthermore, changing the length of chain may be accomplished while the balance case is closed and the beam in motion, so that considerable time is saved in obtaining the final weight.

*Auto-dex and damper attachments* to a balance also facilitate rapid weighing. The auto-dex feature permits moving the pointer scale so that the rest point of the balance will coincide with the zero point on the scale. The adjustment is made rapidly in this way whereas the same adjustment made by means of the nuts on the ends of the balance beam would be time consuming. The damper attachment slows down the oscillation so that the pointer will come to rest after a few excursions. No decrease in accuracy occurs and the speed of weighing is materially increased. Fig. 11 illustrates a chainomatic balance equipped with the auto-dex and damper features. The magnetic damper in the illustration consists of an aluminum plate which moves between the poles of a horseshoe magnet.

**Mass vs. Weight.** Strictly speaking, while mass and weight are terms frequently used synonymously, they actually differ in meaning. Mass refers to the amount of matter in an object referred to a standard mass (platinum-iridium kilogram standard at the International Bureau of Weights and Measures). Weight refers to the force of gravity exerted upon an object due to the attraction between that object and the earth. Gravitational forces vary depending upon geographical location and elevation, so that the weight of an object is variable, while its mass does not vary. However, since it is common to determine the mass of an object by comparing its weight with the weight of a known mass, it is customary to use the term weight in place of mass. For practical purposes,

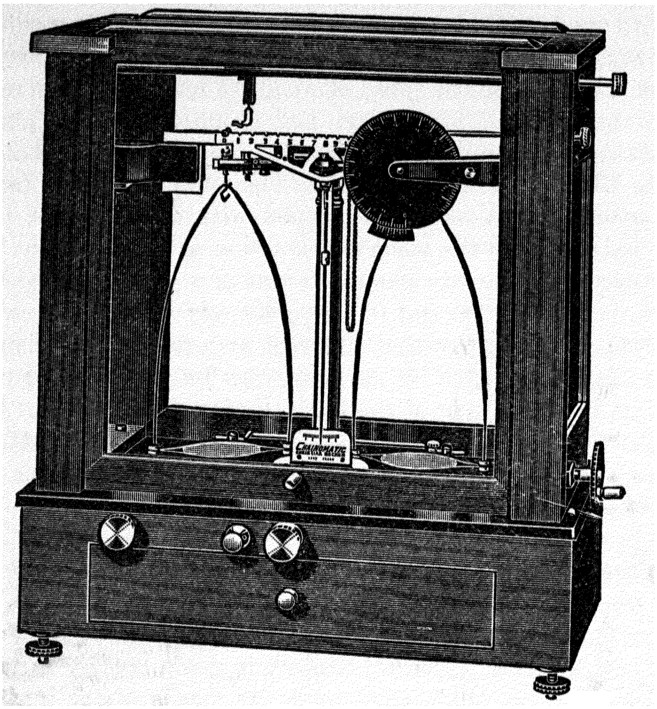

FIG. 11. Magnetically Damped Chainomatic Balance with Movable Pointer Scale (Auto-Dex). (Courtesy of Christian Becker.)

this is correct if, for example, it is understood that "a weight of 10 grams" really means "the mass of an object having a weight equivalent to that of a 10 gram mass."

**Care and Use of the Balance.** The analyst must learn to weigh with accuracy and speed. In learning to weigh, accuracy is emphasized; then, as the procedure becomes familiar, speed will develop as a natural result. The analyst should realize that the balance is an expensive and delicate apparatus and must be handled accordingly. Under no conditions should it be unnecessarily jarred or roughly handled. Some of the precautions to be observed in the use of the balance are as follows:

1. Accurate weighing requires time and consequently should not be attempted when in a hurry.
2. The spirit level or plumb bob inside the balance case indicates whether the balance is level or not. If it is not level, the condition must be corrected before an accurate weighing can be made.

3. Seat yourself or stand directly in front of the balance so that you will be looking directly at the pointer scale, thereby avoiding parallax.

4. Carefully brush off the balance pans with the camel's-hair brush found in your box of weights.

5. Check the rider for its correct weight. See that the rider is either on the exact center of the beam or, if on the rider hook, that it is sufficiently removed so that it will not interfere with the swinging beam.

6. Determine the rest or zero point of the balance. If it varies more than one division on either side of the zero division on the scale, have the instructor make the necessary adjustments.

7. In weighing, first release the beam and then the pans with a slow steady movement. Avoid quick, jerky movements that unnecessarily jar the knife-edges and dull them. The knife-edges are the heart of the balance and, hence, every precaution should be taken to protect them from unnecessary wear. The motion of the beam should be arrested only by the pan arrests; and then only at the time the beam is in a horizontal position.

8. Know the maximum load that the balance is capable of weighing. Most student balances are not designed to weigh objects in excess of 150–200 grams.

9. Indiscriminate wiping of glass apparatus previous to weighing must be avoided or difficulty in weighing will occur due to the electrostatic charge produced on the glass. Allow objects to stand 5 min. or longer after wiping before attempting to weigh them.

10. The object to be weighed is placed in the center of the left-hand pan. Never place objects other than those of metallic, glass or porcelain composition directly upon the pan. Substances to be weighed are usually placed in weighing dishes or on watch glasses. Objects to be weighed *must be at room temperature.* If warmer, they register an apparent loss in weight through the creation of upward air currents around the pan, while if colder, an opposite effect is produced.

11. Always handle the objects to be weighed and the weights with forceps; never touch them with the fingers.

12. Weights are added to the right-hand pan, always starting with the largest weight possible. Arrest the beam and pans when removing or adding weights larger than 0.1 gram. In the case of weights smaller than 0.1 gram, the beam may remain released and the pan arrests alone used.

13. In effecting the final balance by means of the rider, the balance door must be closed to avoid air currents.

14. Add the weights on the balance pan and check against the weights missing from the box.

15. Before leaving the balance, note that the beam and pan arrests are restored, the balance pans are empty, and any material accidentally spilled in the balance has been carefully cleaned out.

**The Balance Rider.** Different balances may require different sized riders. Under no condition, therefore, should a rider be transferred indiscriminately from one balance to another. If the rider is missing, ask the instructor for a new one. To determine the size of the rider required for a balance, note the unit or milligram scale division on the beam directly above the point from which the pans are suspended. If the beam does not extend to this point establish what the division would be if the beam extended that far. This scale division, in milligrams, gives the weight of the rider required and its weight can be checked by weighing it against an appropriate known weight.

The unit rider readings on the beam represent thousandths of a gram (or milligrams), and the divisions between the units ten thousandths of a gram (or tenths of a milligram).

**Determination of the Rest or Zero Point of the Balance.** The rest or zero point of the balance is defined as that point on the scale of the balance at which the pointer would eventually come to rest if permitted to swing freely. With perfect adjustment, this point would coincide with the zero point on the scale. For practical purposes, however, a displacement up to one scale division on either side of the zero mark is permissible. Since the rest point changes with temperature and other conditions, it must be determined each day the balance is used.

The procedure for determining the rest point is as follows: set the balance pans in motion by releasing, first the beam, and then the pan arrests, so that the pointer will swing at least five divisions on one side of the zero mark on the scale. After the pointer has made one complete swing, five consecutive readings are taken, with three representing the maximum pointer swing to the left of the scale, and two to the right of the scale. Each set of readings is averaged and the rest point is the algebraic sum of these averages divided by two. For example:

| Scale divisions to left (−). | Scale divisions to right (+). |
|---|---|
| 5.5 | 5.2 |
| 5.1 | 4.8 |
| 5.0 | 2\| 10.0 |
| 3\| 15.6 | + 5.0 |
| − 5.2 | |
| + 5.0 | |
| 2\| − .2 | |
| − .1 | |

The rest point of the balance is then 0.1 scale division to the left of the actual zero marked on the scale.

If the rest point is off more than one division to the right or left of the zero mark on the scale, have the instructor adjust it and redetermine the rest point. Adjustment is made by adding or subtracting weight at the end of the beam by means of a small adjusting nut.

**Sensitivity of the Balance.** The sensitivity of the balance may be defined as the displacement of the rest point by a 1 mg. load on the balance. It may also be defined as the minimum load which will cause a detectable pointer deflection on the balance scale. Since the sensitivity of the balance varies with the load on the pan, it is helpful to know the sensitivity with various loads. This is especially true if weighing by the method of swings is employed.

To determine the sensitivity of a balance with zero load, first determine the rest or zero point. Then place the rider on the 1 mg. division of the beam and again determine the rest point. The difference between the two rest points gives the sensitivity of the balance in terms of scale division. The sensitivity may also be expressed in terms of the minimum load which is capable of giving a noticeable pointer deflection. Suppose the difference in rest points is four scale divisions. One can, however, with the eye estimate to fifths of a scale division so that there would be twenty such one-fifth divisions in the entire difference of four scale divisions. Since a 1 mg. load caused deflection of the twenty perceptible divisions of the scale, then the smallest load which will cause a perceptible deflection of the pointer is one-twentieth of a milligram and the balance is said to be sensitive to one-twentieth milligram.

Determine the sensitivity of the balance for loads of 0, 3, 5, 10, 20, 50 and 100 grams. Construct a graph in the notebook, plotting the sensitivity as ordinate and load as abscissa.

### METHODS OF WEIGHING

**Weighing by the Ordinary Method of Adjustment.** First determine the rest point of the balance. Then place the object to be weighed in the center of the left-hand balance pan and a weight on the right pan estimated to be approximately the weight of the object. Slowly release the beam and, if necessary, the pan arrests, to determine which way the pointer will swing. If the weight is too heavy, remove it and add the next lighter weight, and so on. When the pointer indicates that the weight added is too light, proceed in the same manner with the next series of weights, and so on until the smallest weight in the box more than counterbalances the object. Remove this weight, close the balance door, and adjust the rider so that the pointer will give the same rest point as was obtained with the balance pans empty. When this occurs, the object to be weighed is exactly counterbalanced by the weights added to the opposite pan plus the rider.

**Weighing by the Method of Swings.** An excellent and rapid method of weighing is by the method of swings. In weighing an object by this method, an approximate weight (± 1 mg.) is obtained and the weight accurate to the fourth decimal place calculated from the sensitivity.

In this method the center of the index plate scale is called 10, the tenth division to the left of center is called zero, and the tenth division to the right of the center is called 20.

Determine the rest point of the empty balance as previously described, using the index scale markings from 0 to 20. For example:

| Pointer excursion to the left | Pointer excursion to the right |
|---|---|
| 2.2 | 17.1 |
| 2.8 | $\underline{16.9}$ |
| $\underline{3.2}$ | $2 \mid \overline{34.0}$ |
| $3 \mid \overline{8.2}$ | 17.0 |
| 2.73 | |

Calculation

17.00

$\underline{2.73}$

$2 \mid \overline{19.73}$

9.87 or 9.9

This rest point is denoted the empty rest point (E.R.P.) of the balance. Check the result obtained by a second empty rest point which should agree with the first within 0.1 of a scale division.

In obtaining the weight of an object, proceed as previously described under weighing by the ordinary method of adjustment until the weight is obtained to the nearest milligram (± 1 mg.). Determine the rest point of the balance under these conditions and denote it as the load rest point (L.R.P.). For example:

| Pointer excursion to the left | Pointer excursion to the right |
|---|---|
| 2.2 | 18.9 |
| 2.8 | 18.5 |
| 3.2 | 2 \| 37.4 |
| 3 \| 8.2 | 18.7 |
| 2.73 | |

Calculation

2.73
18.70
2 | 21.43
10.715 or 10.7

The weights and rider reading used are now recorded. These give the weight of the object to the nearest milligram, i.e., to three decimal places; for example, assume 1.480 grams is the weight obtained to the nearest milligram. In order to obtain the fourth decimal place, the sensitivity of the loaded balance must be determined.

If the L.R.P. was greater than 10, the rider is moved to the right one large beam division (1 mg.); if less than 10, the rider is moved to the left one large beam division. Again obtain a rest point called the sensitivity rest point (S.R.P.), with load of 1.481.

Transfer weights from the balance pan to the box, checking to see that the proper weights were recorded. Remove the rider from the beam and obtain another empty rest point to serve as a check on the first one obtained.

The accurate weight of the object may now be ascertained from the data:

1st E.R.P. 9.9
2nd E.R.P. 9.9
Ave. E.R.P. 9.9

L.R.P. 10.7 (1.480 g. on right pan)
S.R.P. 9.2 (1.481 g. on right pan)
Sensitivity 1.5

Since the L.R.P. was greater than the E.R.P., the object was heavier than the weights used, i.e., heavier than 1.480. The calculated fourth decimal place is thus added to this weight. For example:

$$\text{Weight of the object} = 1.480 + \left(\frac{\text{L.R.P.} - \text{E.R.P.}}{\text{Sensitivity}}\right) \times .001 =$$

$$1.480 + \left(\frac{10.7 - 9.9}{1.5}\right) \times .001 = 1.4805 \text{ grams.}$$

If the L.R.P. had been less than the E.R.P., it would have indicated that weights used were heavier than the object and the calculated fourth decimal place would have been subtracted rather than added. For example:

$$\begin{array}{rll} \text{Ave. E.R.P.} = & 10.0 & \\ \text{L.R.P.} = & 9.9 & (2.001 \text{ g. on right pan}) \\ \text{S.R.P.} = & \underline{11.5} & (2.000 \text{ g. on right pan}) \\ \text{Sensitivity} & 1.6 & \end{array}$$

$$\text{Weight of the object} = 2.001 - \left(\frac{\text{E.R.P.} - \text{L.R.P.}}{\text{Sensitivity}}\right) \times .001 =$$

$$2.001 - \left(\frac{10.0 - 9.9}{1.6}\right) \times .001 = 2.0009 \text{ grams.}$$

When using this method of weighing it is advantageous to determine the sensitivity of the balance with varying loads and to construct a graph so that the sensitivity with any load may be ascertained easily. This eliminates the necessity of determining the sensitivity rest point with every weighing.

**Weighing by Substitution.** When an absolute weight is required, as is true in calibration and standardization work, weighing by substitution must be employed to obtain the correct values.

Slight inequalities in the length of the balance arms or beam error are common in laboratory balances and will cause an error in obtaining an absolute weight by any of the previously discussed methods of weighing. This may be demonstrated readily by counterbalancing one weight on one balance pan by an identical weight on the other balance pan. If the two weights are now interchanged on the pans, it frequently happens that they no longer counterbalance each other. Ordinarily this does not introduce an error in weighing since in most cases we are simply determining differences when weighing, e.g., the weight of a crucible alone and its weight containing a precipitate to determine the weight of precipitate, etc. Since the precipitate has so small an absolute weight, the error introduced by inequalities in the balance arms is too small to be detected on the ordinary balance.

In weighing by substitution, the object is placed on the right-hand balance pan and exactly counterbalanced by tares placed on the left-hand pan plus the rider. The object is then removed and weights substituted for it until a balance is again effected. The weights are then exactly equivalent to the weight of the object, irrespective of any difference in the balance arms.

## BALANCE WEIGHTS

All weights used in the major nations of the world must agree, within certain tolerances, with the international kilogram kept at the International Bureau of Standards near Paris, France. The United States has two copies of the original standard which are used by the Bureau of Standards at Washington to check the working standards of the Bureau. The working standards are used by the Bureau to check the weights submitted to it for calibration. All laboratories should possess a set of high precision weights calibrated by the National Bureau of Standards for use as primary laboratory standards, against which all other weights used in the laboratory may be calibrated.

The Bureau of Standards has divided weights into two classes: Those used for commercial purposes and those used for scientific purposes. The tolerances (or errors) permitted on weights used for commercial purposes are much greater than for the weights used for scientific purposes. Weights used for scientific purposes are further divided into three classes depending upon construction and tolerances.

Weights of the highest precision are the Class M weights. The gram weights are of a one-piece design made of hard non-magnetic, non-porous metals resistant to corrosion. If the weights are made of brass or bronze, they must be plated with gold, platinum or some other suitable tarnish-proof metal. The fractional weights should be constructed of platinum, although aluminum may be used for weights of 20 mg. or less. The tolerance allowed varies with the size of the weight and in general is low (see Table 1). Weights of this class are used only as primary standards for the checking of other weights.

Class S weights are used for accurate weighing in scientific work. The gram weights may be of a one-piece or two-piece design, constructed from brass or bronze, and plated with gold, platinum, chromium, or some other tarnish-proof metal or else lacquered.

The fractional weights are made of platinum to the 50 mg. piece, below which aluminum may be used. The tolerances for this class of weights are the same as for the Class M weights.

Weights used for routine laboratory weighing and student work usually fall in the S-2 class. These weights conform to the same specifications for construction as the Class S weights, except that all the fractional weights may be made of aluminum. Tolerances for this class are five times those of the Class S weights (see Table 1).

TABLE 1. ALLOWABLE TOLERANCES FOR SCIENTIFIC WEIGHTS

| Denomination | Class M (milligrams) | Class S (milligrams) | Class S-2 (milligrams) |
|---|---|---|---|
| 100 g. | 0.5 | 0.5 | 2.5 |
| 50 g. | 0.3 | 0.3 | 1.5 |
| 20 g. | 0.2 | 0.2 | 1.0 |
| 10 g. | 0.15 | 0.15 | 0.75 |
| 5 g. | 0.15 | 0.15 | 0.75 |
| 2 g. | 0.10 | 0.10 | 0.50 |
| 1 g. | 0.10 | 0.10 | 0.50 |
| 500 mg. | 0.05 | 0.05 | 0.25 |
| 200 mg. | 0.05 | 0.05 | 0.25 |
| 100 mg. | 0.05 | 0.05 | 0.25 |
| 50 mg. | 0.03 | 0.03 | 0.15 |
| 20 mg. | 0.03 | 0.03 | 0.15 |
| 10 mg. | 0.02 | 0.02 | 0.10 |
| 5 mg. | 0.02 | 0.02 | 0.10 |

Weights should always be kept in their proper place, in a closed box, except when in use. Weights should never be touched with the hands but should be handled with a forceps, preferably with one that is ivory tipped.

**Calibration of Balance Weights by Direct Comparison with a Standard Set of Weights.** A high-grade set of weights calibrated by the United States Bureau of Standards should be used as the standard or reference set. The Bureau of Standards will certify sets of high-grade weights for use as reference sets upon payment of a fee to cover the cost of calibration. Another set of weights of any grade should also be available as tares.

Place the 50 gram weight from the calibrated reference set on the right balance pan, a 50 gram weight as tare on the left pan, and effect a balance with the aid of the rider. Then substitute the 50 gram weight to be calibrated for the reference weight and again effect a balance with the use of the rider. The difference in rider readings is the difference in weight between the reference weight and the weight to be calibrated. For example, suppose the rider reading with the reference weight on the right pan was +.0005. If, upon substituting the weight to be calibrated, the rider reading was +.0003, it would indicate that the weight to be calibrated was .0005 −.0003 or .0002 gram heavier than the reference weight. If the reference weight was exactly 50.0000 grams, then the weight to be calibrated would be 50.0002 grams and its correction would be +.0002 gram. On the other hand, if the rider reading with the weight to be calibrated had been +.0008, it would have indicated that the weight was .0008−.0005 or .0003 gram lighter than the reference weight. Again, if the reference weight was exactly 50.0000 grams, the weight to be calibrated would be 49.9997 grams and its correction would be −.0003 gram.

TABLE 2. CALIBRATION OF WEIGHTS BY DIRECT COMPARISON

| Weight To Be Calibrated (grams) | Rider Reading with Standard Weight (milligrams) | Rider Reading with Weight To Be Calibrated (milligrams) | Actual Weight of Standard (grams) | Calibrated Weight (grams) | Correction (milligrams) |
|---|---|---|---|---|---|
| 50. | +2.7 | +2.5 | 50.0000 | 50.0002 | +0.2 |
| 20. | +1.0 | +0.6 | 19.9998 | 20.0002 | +0.2 |
| 20.* | +1.0 | +1.1 | 19.9998 | 19.9997 | −0.3 |
| 10. | +0.7 | +0.3 | 10.0000 | 10.0004 | +0.4 |
| 5. | −0.1 | −0.1 | 5.0000 | 5.0000 | 0.0 |
| 2. | 0.0 | 0.0 | 2.0000 | 2.0000 | 0.0 |
| 2.* | 0.0 | +0.2 | 2.0000 | 1.9998 | −0.2 |
| 1. | −0.1 | −0.1 | 1.0000 | 1.0000 | 0.0 |
| .5 | 0.0 | 0.0 | .5000 | .5000 | 0.0 |
| .2 | 0.0 | +0.1 | .2000 | .1999 | −0.1 |
| .2* | 0.0 | −0.1 | .2000 | .2001 | +0.1 |
| .1 | 0.0 | −0.1 | .1000 | .1001 | +0.1 |
| .05 | 0.0 | 0.0 | .0500 | .0500 | 0.0 |
| .02* | 0.0 | 0.0 | .0200 | .0200 | 0.0 |
| .02 | 0.0 | 0.0 | .0200 | .0200 | 0.0 |
| .01 | 0.0 | 0.0 | .0100 | .0100 | 0.0 |

Using this procedure, compare all the weights in the set with their respective reference Bureau of Standards calibrated weights and indicate their true values and corrections. Table 2 illustrates the calibration of a set of weights by this method, indicating the tabulated data and the corrections found for each weight.

**Calibration of Balance Weights by Relating All Weights in the Set to Each Other.** In the event a standardized reference set of weights is not available, the weights may be calibrated by determining their relative values to each other (modification of the Richards[1] method). This permits the interchange of any weights in the set since all the weights are related to each other. For example, such calibration insures that the 1 gram weight is ten times the mass of the 0.1 gram weight, one-half of the mass of the 2 gram weight, one-tenth of the mass of the 10 gram weight, etc. However, it does not insure that the 1 gram weight has a mass of exactly 1 gram or the 10 gram weight a mass of exactly 10 grams. To determine the absolute values, direct comparison with a standard set of weights should be resorted to. For all practical purposes, weights calibrated in terms of each other are accurate for analytical purposes since we obtain the weight of one substance with reference to the weight of another.

*Principle.* One weight is selected as a final standard, for example, the 10 gram weight. Another weight, the 5 or 10 mg. weight is selected as a preliminary standard. The entire set is weighed in terms of the preliminary standard and then calculated in terms of the final standard.

*Procedure.* If the set contains a 5 mg. weight, select it as a preliminary standard and assume its weight to be exactly 0.0050 gram. Place a 10 mg. tare on the left balance pan, the 5 mg. weight on the right, and effect a balance with the rider. Record the reading of the 5 mg. weight plus rider. Remove the 5 mg. weight and place the 10 mg. weight to be calibrated on the right balance pan. Again effect a balance with the rider and note the reading of the 10 mg. weight plus rider. The difference between the two readings will determine the correction to be applied to the 10 mg. weight in terms of the preliminary standard. Apply the correction found and denote the weight of the 10 mg. weight in terms of the preliminary standard. This weight is now a standard and is used together with the 5 mg. weight and rider to calibrate the 20 mg. weight in terms of the preliminary standard. Repeat this process for all the weights in the set and record the results as in Table 3.

*Calculations in Terms of the Preliminary Standard (Table 3).* The 10 mg. tare is balanced by the 5 mg. weight with the rider at 0.0051 gram. The same tare is balanced by the 10 mg. weight with the rider at 0.0001 gram. In other words, the 10 mg. piece has the same weight as the rider reading plus the 5 mg. standard which is assumed to be accurate, therefore the 10 mg. weight is considered to weigh 0.0100 gram. The same is true for the 20 mg. weights.

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[1] Richards, *J. Am. Chem. Soc.*, 22, 144 (1900).

The 50 mg. tare is exactly balanced by the two 20 mg. and the 10 mg. weights. Upon substitution of the 50 mg. weight it will be noted that a −.0001 gram rider reading is required to effect a balance with the tare. This indicates that the 50 mg. weight is .0001 gram heavier than the combined weight of the two 20 mg. and one 10 mg. pieces. Since the 20 and 10 mg. weights were previously found to be exactly correct in terms of the preliminary standard, then the 50 mg. piece has a weight of .0501 gram. Similarly, the 100 mg. piece is exactly equivalent to the combined weight of the 10, 20 and 50 mg. pieces. These combined weights total .1001 gram, therefore, the 100 gm. piece is considered to weigh .1001 gram in terms of the preliminary standard. This same reasoning is used to calculate all the weights of the set in terms of the preliminary standard 5 mg. weight.

TABLE 3. CALIBRATION OF WEIGHTS BY THE MODIFIED RICHARDS METHOD

| Weight To Be Calibrated (grams) | Preliminary Standardized Weights Used | Rider Reading with Preliminary Standard | Rider Reading with Weight To Be Calibrated | Weight in Terms of Preliminary Standard (grams) | Aliquot Part of Preliminary Standard (grams) | Weight in Terms of Final Standard (grams) | Correction (milligrams) |
|---|---|---|---|---|---|---|---|
| .01 | .005 | +.0051 | +.0001 | .0100 | .0100 | .0100 | 0.0 |
| .02 | .005 + .01 | +.0051 | +.0001 | .0200 | .0200 | .0200 | 0.0 |
| .02* | .02 | +.0001 | +.0001 | .0200 | .0200 | .0200 | 0.0 |
| .05 | .02 + .02 + .01 | .0000 | −.0001 | .0501 | .0500 | .0501 | +0.1 |
| .1 | .02* + .02 + .05 + .01 | −.0001 | −.0001 | .1001 | .1000 | .1001 | +0.1 |
| .2 | .02* + .02 + .05 + .01 + .1 | −.0002 | +.0001 | .1999 | .2001 | .1998 | −0.2 |
| .2* | .2 | +.0001 | −.0003 | .2003 | .2001 | .2002 | +0.2 |
| .5 | .1 + .2* + .2 | −.0002 | +.0001 | .5000 | .5000 | .5000 | 0.0 |
| 1. | .1 + .2 + .2* + .5 | .0000 | .0000 | 1.0003 | 1.0003 | 1.0000 | 0.0 |
| 2. | .1 + .2* + .2 + .5 + 1. | −.0001 | .0000 | 2.0005 | 2.0005 | 2.0000 | 0.0 |
| 2.* | 2. | .0000 | +.0003 | 2.0002 | 2.0005 | 1.9997 | −0.3 |
| 5. | 2. + 2.* + 1. | +.0004 | +.0001 | 5.0013 | 5.0013 | 5.0000 | 0.0 |
| 10. | 1. + 2. + 2.* + 5. | +.0007 | +.0003 | 10.0027 | 10.0027 | 10.0000 | 0.0 |
| 20. | 1. + 2. + 2.* + 5. + 10. | +.0010 | +.0008 | 20.0052 | 20.0054 | 19.9998 | −0.2 |
| 20.* | 20. | +.0008 | +.0012 | 20.0048 | 20.0054 | 19.9994 | −0.6 |
| 50. | 20. + 20.* + 10. | +.0022 | +.0020 | 50.0129 | 50.0135 | 49.9994 | −0.6 |

*Calculation in Terms of the Selected Final Standard.* Since the larger weights are relatively more accurate than the smaller ones, the final standard is selected from one of the larger weights—say the 10 gram weight. The 10 gram weight in terms of the preliminary standard weighs 10.0027 grams. The 5 gram weight should be one-half as heavy as the 10 gram, or, in terms of the preliminary standard, 5.0013 grams. Since the 5 gram weight does weigh 5.0013 grams in terms of the preliminary standard, its calculated weight in terms of the final 10 gram standard is exactly 5.0000 grams. The 20 gram weight should be twice as heavy as the 10 gram weight, or in terms of the preliminary standard should weigh 20.0054 grams. Since the 20 gram weight was found to weigh 20.0052 grams, it is .0002 gram too light in terms of the final standard and its calculated weight is 19.9998 grams. All the weights in the set are calibrated in terms of the final standard 10 gram weight by this method. Table 3 illustrates the calibration of a set of weights by this method indicating the tabulated data and the corrections found for each weight.

**Adjustment of Analytical Weights.** If the calibration of the weights is to mean anything, the corrections must be applied thereafter for each weight used in a weighing. This is time consuming and also gives a chance for errors to be made. The adjustment of weights to a desired tolerance (0.05 to 0.1 mg.) is to be recommended since it eliminates the application of any correction for the weights.

The gram pieces (except M class weights which should not require adjustment) consist of a base and a handle which screws into the base. The hole in the base into which the handle screws frequently contains small pieces of metal filler which have been added to bring the weight within the manufacturer's tolerances for the particular class of weight. If the weight is too heavy, the handle is unscrewed and either the required amount of metallic filler removed or sufficient metal filed off the screw end of the handle to make the weight exactly as designated. If the weight is too light, small pieces of metallic aluminum or zinc may be added to the weight until the required amount has been determined, then these pieces are dropped into the hole in the base and the handle screwed on.

Fractional weights may be burnished to the required weight if too heavy. If too light, it is best to replace them with new weights which will come within the tolerances prescribed.

## WEIGHING OF SAMPLES

**Weighing Sample by Difference.** This procedure for obtaining a sample weight may be used any time but must be employed whenever the sample material is readily affected by the atmosphere, i.e., will gain or lose weight on exposure to the atmosphere. The material to be analyzed is placed in a stoppered sample tube or covered weighing dish. A weight is obtained on the container, tube, or dish of material. A sample portion of the material is then transferred from the container to a flask or beaker by pouring, or with the aid of a spatula, taking care that all material is thoroughly brushed off the spatula to avoid loss of sample, and the container with the remaining material again weighed. The difference between the two weights is the weight of sample removed. In this method of securing the sample weight, the sample is exposed to the air only for the very brief time that the actual transfer of the sample from the container to the beaker takes place.

**Weighing Sample Directly.** If the sample material is not affected by exposure to the atmosphere, it may be weighed directly. Counterpoised watch glasses or weighing dishes are useful vessels into which samples may be weighed rapidly. It is simply necessary to transfer sufficient of the sample material to the counterpoised watch glass or dish on the balance pan, add weights to effect a balance, and the weight added is the weight of the sample.

**Weighing a Predetermined Sample Weight.** Frequently it is desirable to weigh a definite predetermined sample weight in order to simplify the calculations involved in the determination. In this instance, using counterpoised watch glasses or dishes, place balance weights equivalent to the weight of sample desired on the right balance pan and add sufficient sample material to the watch glass or dish on the left balance pan until a balance is effected. This weighing procedure requires experience for rapid weighing since the beginner will spend considerable time adding to and abstracting sample material from the dish with a spatula before a balance is obtained. However, with practice, weighings may be made quite rapidly and the somewhat longer weighing time is compensated for by the less complicated calculations involved.

**Use of Aliquot Parts to Obtain Sample Weight.** If the desired predetermined sample weight is small, there is the possibility of an appreciable error in weighing. Furthermore, when replicate determinations are made, a number of careful and tedious weighings are required. These difficulties may be eliminated to a large extent, if the sample is soluble, by the application of the principle of aliquot parts.

Suppose, for example, that a 0.1000 gram sample of a soluble substance is desired and replicate determinations are to be made. Weigh accurately a 1.0000 gram sample of the material and transfer it to a 250.0 ml. volumetric flask. Any error in weighing a 1-gram sample will be proportionately less than that when weighing a 0.1-gram sample. Dissolve the sample in water and dilute to volume. The material is then homogeneously dispersed in the solution and each milliliter contains 1/250th of the total weight of the substance dissolved or 0.0040 gram. One tenth (25 ml.) of the solution would contain 25 × 0.0040 gram or 0.1000 gram. Therefore, if a 25-ml. aliquot (one tenth of the volume) of the solution is removed for a sample, this aliquot will contain one tenth of the original sample weight or in this case 0.1000 gram of sample.

Since the fraction of the volume of solution (aliquot) removed for analysis contains the same fraction of the weight of original material put into the solution, several aliquots may be removed easily for analysis from a single solution; a procedure which is much more rapid and, in many instances, more accurate than weighing out the same number of individual samples. A further advantage in the use of aliquot parts is evident when materials difficult to mix are analyzed. In this instance, a large sample of the material will be more representative of the whole than a smaller sample. The use of a large sample, which upon solution is thoroughly mixed, will permit the removal of homogeneous aliquots for analysis.

# CHAPTER IV

# GRAVIMETRIC DETERMINATIONS

## THE DETERMINATION OF SULFUR IN A SOLUBLE SULFATE

The soluble sulfate is dissolved in water, acidified with hydrochloric acid, and the sulfate precipitated as insoluble barium sulfate with barium chloride solution. The barium sulfate is filtered from the solution, washed free from impurities, dried, ignited, cooled, weighed, and the sulfur content of the sample calculated.

**Reagents.**

1. *Dilute hydrochloric acid solution (1:4)* prepared by diluting 1 volume of concentrated hydrochloric acid with 4 volumes of water.
2. *A 5 per cent barium chloride solution* with a specific gravity of 1.037. Dissolve 5 grams of barium chloride ($BaCl_2 \cdot 2H_2O$) in 95 grams of water.
3. *A silver nitrate solution* prepared by dissolving 3 grams of silver nitrate in water and diluting to a volume of 100 ml.

**Preparation of Crucibles.** Thoroughly clean two porcelain crucibles and see that they are marked (p. 26). Place the crucibles on clean clay triangles supported on ring stands and heat for 30 min. to the full heat of the burner. Place the heated crucibles in a desiccator to cool, being careful that the heated air in the desiccator does not blow off the cover (read carefully p. 11). Cool the crucibles for 20–30 min. and weigh. Heat again and reweigh. Continue heating, cooling and reweighing the crucibles until two consecutive weighings on a crucible are not more than 0.2 mg. apart. The crucibles are then considered to be at a constant weight. If a muffle furnace operating at 550°–650° C. is available, the crucibles may be heated to a constant weight in it rather than over a burner.

**Weighing the Sample** (read p. 45). Dry a shallow layer of the sulfate sample in a flat type weighing bottle for one hour at 105° C. Cover the dish and cool in a desiccator. Weigh the dish and contents and record the weight in your notebook. Carefully transfer, with the aid of a spatula, a portion of the sample between 0.4 and 0.7 gram into a previously cleaned and numbered 400 ml. beaker. Again weigh the dish and contents and record the weight. The difference between the two weighings represents the weight in grams of sample number 1. Repeat the same procedure for sample number 2. Mark the beakers with the sample numbers.

**Solution and Precipitation.** Using a graduated cylinder, add 200 ml. of distilled water to each beaker and stir until the sample is dissolved. Add 2 ml. of dilute hydrochloric acid (1:4) to prevent the precipitation of barium as the carbonate, phosphate, chromate, etc., which are insoluble in neutral solution but soluble in acid solution. Avoid too much hydrochloric acid as barium sulfate is somewhat soluble in this acid.

Assuming the sample to be pure sodium sulfate, calculate the milliliters of 5 per cent $BaCl_2 \cdot 2H_2O$ solution (specific gravity 1.037) required to precipitate all the sulfur present in the sample. To insure an excess of precipitating agent (so that precipitation is complete and for common-ion effect on solubility) add a 10 ml. excess of the barium chloride solution to the calculated amount.

Heat the dissolved and acidified sample to boiling and add dropwise, with constant stirring, the amount of barium chloride solution calculated to precipitate all the sulfur and also give an excess of precipitating agent. Cover the beaker with a watch glass and continue the heating just below the boiling point for 15 min. or digest on the steam bath for one hour. At the conclusion of the digestion period, allow the precipitate to stand for at least one-half hour but preferably overnight before filtering. The heating and digestion insures the formation of large crystals.

**Filtration and Washing.** Fold and properly fit a 11 cm. quantitative ashless filter paper into each of two funnels suspended on a funnel support (see p. 22). Place a clean 400 ml. beaker underneath the funnel and in contact with the end of the funnel stem. Decant the supernatant liquid from the precipitated sample upon the filter. This is accomplished by holding a stirring rod tightly against the lip of the beaker and so directing the liquid down the rod and upon the filter.

In any filtering operation of this kind, the liquid should never completely fill the paper but should always be kept one-fourth to one-half inch below the upper edge of the filter. If the filtrate comes through turbid, it should be refiltered through the same filter paper.

When all the supernatant liquid has been transferred to the filter, wash the barium sulfate precipitate remaining in the beaker several times by decantation. Use 15 ml. of hot water for each washing and transfer the entire wash water upon the filter before washing with the next 15 ml. portion.

Finally, transfer the entire precipitate of barium sulfate to the filter using a rubber tipped stirring rod and a stream of hot water from the wash bottle to remove the last particles sticking to the sides of the beaker. Wash the precipitate and filter with numerous small portions of hot water until a test portion of the filtrate treated with silver nitrate solution, acidified with nitric acid, gives no test for chlorides. Since chlorides constitute the greatest share of the impurities present, it is assumed that all impurities will have been removed when the precipitate has been washed free from chlorides.

**Ignition and Weighing.** If the filtration has been completed near the end of the class period, the filter may be folded over the precipitate and placed in a weighed marked crucible and allowed to dry until the next class period. However, the filter and precipitate may be dried and ignited immediately. In this event, fold the filter over the precipitate and place in a weighed and marked crucible. If any barium sulfate precipitate has splashed on the funnel above the filter, wipe off carefully with a piece of moistened quantitative filter paper and add it to the crucible. Partly cover the crucible with a cover and incline the crucible on a triangle, supported on a ring stand. Apply a gentle heat to the base of the crucible and, as the material dries, gradually increase the heat applied until the filter has charred. If the filter and precipitate have been previously dried, they are ignited in the same manner but require less care during the ignition.

After the paper has been thoroughly charred, the crucible covers are removed and the heating continued until no more carbon particles are in evidence. If a muffle furnace is available for the ignition, the crucible and charred precipitate are placed in the furnace held at a dull red heat (550°–650° C.) until free from carbon. The crucible and contents are then cooled in a desiccator and weighed. Repeated reheatings and weighings are made until constant weights are obtained. From the results obtained, calculate the percentage of sulfur present in the sample, and the per cent error between replicates.

## THE DETERMINATION OF CHLORIDE

The sample is dissolved in water and acidified with nitric acid. Silver nitrate is added to precipitate all the chloride as insoluble silver chloride. The silver chloride precipitate is filtered off by means of a Gooch crucible containing an asbestos mat, washed free from impurities, and dried to constant weight at 105°–110° C. From the weight of silver chloride obtained calculate the percentage of chloride in the sample.

**Reagents.**

1. *A silver nitrate solution* containing 0.030 gram of silver nitrate per milliliter (see p. 47).
2. *A hydrochloric acid solution (1:4)* (see p. 47).
3. *An approximately 20 per cent nitric acid solution* prepared by adding 20 ml. of concentrated nitric acid to 72 ml. of water.

**Procedure.** Two marked Gooch crucibles are prepared with asbestos mats as previously described on page 24. The crucibles are dried in an oven at 105°–110° C. for one hour, then cooled and weighed. Further reheatings are made in the drying oven for 30-min. intervals until the crucibles attain a constant weight.

While the Gooch crucibles are drying to constant weight, secure the sample for the chloride determination from the instructor and weigh two samples of 0.2–0.3 gram each into two 400 ml. beakers. Dissolve each sample in 150 ml. of distilled water (free from chloride) and add 1 ml. of 20 per cent nitric acid.

Assuming each sample to be pure sodium chloride, calculate the volume of silver nitrate solution (1 ml. containing 0.030 gm. of silver nitrate) required to precipitate all the chloride present. Slowly, with constant stirring, add the calculated quantity of silver nitrate solution plus a 5 ml. excess to the acidified solution, heated almost to boiling. Continue the heating to just below the boiling point in the absence of direct sunlight in order to flocculate the precipitate. When this has occurred, the precipitate should settle out leaving a clear supernatant liquid. Add a few drops of the silver nitrate solution to the supernatant liquid and if no turbidity results, assume that all the chloride has been precipitated.

Place a marked and weighed Gooch crucible in the adapter mounted on a suction flask. With the suction turned on, carefully moisten the pad of the filter thoroughly with distilled water. Then carefully pour the supernatant liquid from the chloride precipitation along a stirring rod held, at first, well down into the crucible to prevent the force of the liquid from disturbing the crucible mat. Decant all the supernatant liquid through the filter without permitting the crucible to become empty during the process. Wash the precipitate in the beaker several times by decantation with 15 ml. portions of hot acidified wash water (the acidified wash water is made by adding 5 drops of dilute nitric acid to 200 ml. of distilled water). By means of a stirring rod and a wash bottle containing hot acidified wash water, transfer the precipitate to the filter pad of the Gooch crucible.

Wash the crucible and precipitate with small portions of the hot acidified wash water, allowing each portion to drain before washing with the next. The washing is continued until the filtrate no longer gives a test for silver ion. (Test by adding dilute hydrochloric acid to a fresh portion of the filtrate acidified with nitric acid. No turbidity denotes the absence of silver ion which is an indication that the washing is complete.)

To facilitate drying, wash the crucible and precipitate once with 95 per cent ethyl alcohol, being careful to use an empty suction flask for this washing Remove the crucible from the adapter and carefully wipe the outside of the crucible with a clean, dry cloth. Dry in an oven at 105°–110° C. for one hour, cool, and weigh. Reheat for 30-min. periods until constant weight is obtained. Calculate the percentage of chloride in each sample and obtain the mean percentage. Also calculate the per cent of error between replicates.

# PART III

# VOLUMETRIC ANALYSIS

## CHAPTER V

## VOLUMETRIC METHODS, APPARATUS AND SOLUTIONS

In the volumetric methods of analysis, the amount of an element or compound present in a sample is ascertained by calculation from the volume of a dissolved reagent of known concentration required to complete a definite reaction. The general procedure is to add measured volumes of a reagent of known concentration to a certain weight or volume of sample until the reaction is complete. An indicator or other visible means is used to indicate the completion of the reaction, and the procedure is known as a titration.

Volumetric methods differ among themselves in the nature of the reactions involved. Three common types of volumetric methods are:

1. *Neutralization.* Methods used in determining the acidity or basicity of a solution and therefore called methods of acidimetry and alkalimetry.
2. *Oxidation and Reduction.* Methods involving reactions between oxidizing and reducing substances of which the most important are the permanganate, dichromate, ceric sulfate, and iodometric methods.
3. *Precipitation.* Methods in which the substance analyzed for is converted to a precipitate, for example, the Volhard method for chloride.

In general, the fundamental reactions involved in these processes are of the reversible type, yet they must go practically to completion in order to be used as the basis for a quantitative method. Neutralization reactions go to completion due to the small amount of ionization of one of the reaction products, namely, water. Oxidation and reduction reactions proceed to completion because of the relative potentials of the oxidizing and reducing substances under specific experimental conditions. Volumetric precipitation methods go to completion because one of the reaction products forms an insoluble precipitate.

**Units of Volume.** The standard unit of volume is the liter. It is defined as the volume occupied by one kilogram of water at its maximum density. Most volumetric apparatus is graduated into thousandths of a liter, expressed as milliliters. Previous to the selection of a standard meter and a standard kilogram by the International Bureau of Weights and Measures in 1889, the unit of volume was the cubic decimeter. This was the volume occupied by a cube 10 cm. on a side or 1000 cu. cm. (c.c.). Since the liter and cubic decimeter are not absolutely identical (1 liter is equivalent to 1.000027 cu. dm. (cubic decimeters)) and since the present accepted unit of volume is the liter, it is preferable to use the terms liter and milliliter rather than cubic decimeter and cubic centimeter in volumetric work.

The Mohr liter is the volume occupied by a kilogram of water when weighed in air with brass weights at a temperature of 17.5° C. The normal liter is related to the Mohr liter as 1000:1002.3.

**Volumetric Apparatus.** The United States Bureau of Standards has suggested that 20° C. be the standard temperature at which volumetric apparatus should be used. Etched on each piece of volumetric apparatus is a statement of the volume contained or delivered for that particular piece of apparatus at 20° C. If the apparatus is used at another temperature, it must be recalibrated for that particular temperature.

Volumetric measurements are made by means of flasks, burettes, pipettes and cylinders. Graduated cylinders and graduated Mohr pipettes are employed in making rough measurements, whereas, for accurate work graduated flasks, burettes and transfer pipettes must be used. Since the accuracy of quantitative volumetric methods is dependent largely upon the accuracy with which volumes can be measured, it is essential to be careful in the selection and use of the proper volumetric apparatus.

**Volumetric Flasks.** These flasks are usually calibrated to contain a definite volume of water at 20° C., although some are also calibrated to deliver a definite volume. Volumetric flasks are cleaned with cleaning solution followed by a thorough rinsing with water. Drops of water adhering to the sides of the flask indicate that it is not "clean" whereupon the cleaning procedure is repeated. A glass-stoppered volumetric flask, when not in use, should have a piece of paper placed around the stopper before inserting it into the flask to prevent the "freezing" or sticking of the stopper.

*Calibration of a Volumetric Flask.* Place the clean, dry volumetric flask, including stopper, on the left-hand balance pan and counterpoise the flask with tares until a rest point is obtained near the center of the index scale. If the volumetric flask is larger than 100 ml., a balance of sufficient capacity must be employed, i.e., from 500 to 1,000 grams capacity. Secure the pan supports and raise the beam arrest. Remove the flask, and substitute for it sufficient weights to give the same rest point as was obtained with the flask. Raise the pan and beam arrests, record the weights, and then remove the weights and tares from the balance pans.

Very carefully fill the flask to the mark with distilled water at room temperature. This is accomplished by using first a long-stemmed funnel and then a pipette. It is preferable that no water contact the neck of the volumetric flask above the calibration mark. If this does occur, remove the water with a piece of filter paper wrapped around a stirring rod. Note and record the temperature of the water in your notebook.

Stopper the flask and weigh by the method of substitution, which was employed in determining the weight of the dry flask. From the weight of the water and its temperature, calculate the volume of water contained in the flask. For convenience in calculations, the weight of 1 ml. of water weighed in air with brass weights and corrected for buoyancy is given for various temperatures in Table 4.

TABLE 4. WEIGHT IN AIR OF 1 ML. OF WATER WEIGHED WITH BRASS WEIGHTS AND CORRECTED FOR BUOYANCY

| Temperature °C. | Weight of 1 Ml. of Water | Temperature °C. | Weight of 1 Ml. of Water |
|---|---|---|---|
| 11 | .9983 | 21 | .9970 |
| 12 | .9982 | 22 | .9968 |
| 13 | .9981 | 23 | .9966 |
| 14 | .9980 | 24 | .9964 |
| 15 | .9979 | 25 | .9962 |
| 16 | .9978 | 26 | .9959 |
| 17 | .9977 | 27 | .9957 |
| 18 | .9975 | 28 | .9954 |
| 19 | .9974 | 29 | .9952 |
| 20 | .9972 | 30 | .9949 |

**Burettes.** These are graduated tubes usually of 25 or 50 ml. capacity, graduated in tenths of a milliliter. They measure volumes delivered and are especially useful in titration procedures.

Burettes when in use *must be clean* in order to obtain accurate results. Drops of liquid adhering to the side of the burette when it drains indicate that the burette is dirty. To clean, use a burette brush with soap and water. Rinse thoroughly with water followed by cleaning solution. Rinse again with water and finally with the solution to be measured. In filling the burette, add enough solution to fill the entire length of the burette. This will insure clearing the burette tip of air bubbles when the excess solution is drained to the zero mark of the burette. When reading the burette it is necessary to have the eyes on the same level with the meniscus of the solution to avoid an incorrect reading due to parallax. Burettes are graduated to read units and tenths of a milliliter; hundredths of a milliliter may be estimated.

A 50 ml. burette should have a tip of such a bore that it will drain in not less than 90 sec. and not longer than 180 sec. This will insure drainage along the sides of the burette as rapidly as the burette empties, permitting the correct reading of the burette as soon as the stopcock is closed. Drainage for a period longer than 180 sec. consumes too much time to be practical. If the burette drains too rapidly, ask the instructor to remedy the situation.

*Calibration of a Burette.* Insure that the burette to be calibrated drains in the correct length of time, that it is absolutely clean and drains freely, and that the stopcock is properly greased so that no leakage occurs.

Fill the burette with distilled water at room temperature and record the temperature in your notebook. Allow the burette to stand for 3–5 min. to allow any air bubles in the water to escape. During this time obtain the weight of a tall form, glass-stoppered weighing bottle with a capacity of 75–100 ml.

Starting from 0.0 ml. on the burette, run 5 ml. of water into the weighing bottle, touch the tip of the burette to the side of the

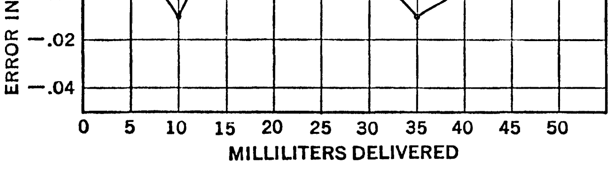

FIG. 12. Calibration Curve for a Burette.

weighing bottle, stopper and weigh to the nearest milligram. Read the volume of water delivered from the burette after standing 30 sec., estimating the hundredths of a milliliter. Repeat for each 5 ml. portions of the burette.

Calculate the actual volume delivered for each portion from the weight of water delivered and the temperature, using Table 4. Subtract the apparent volumes obtained in the burette readings from the actual volumes to obtain the burette correction for each portion. Duplicate observations should agree within 0.04 ml. The corrections are usually plotted as in Fig. 12 to facilitate their use when employing the burette.

**Transfer Pipettes.** The ordinary pipettes used for accurate volumetric measurements are transfer pipettes (usually bulb pipettes) calibrated to deliver 1, 5, 10, 25, 50, 100 or 200 ml. at 20° C. If they are to be used at some other temperature, they must be recalibrated. Absolute cleanliness of pipettes is essential, as it is with all volumetric apparatus, and a thorough cleaning with cleaning solution followed by a water rinsing should make the pipette drain freely without liquid adhering to the sides.

The most important factor in the correct use of the pipette is the matter of draining. After the bulk of the liquid has drained from the pipette there is always a slight accumulation of liquid in the tip. Various procedures have been suggested to insure the delivery of the same volume of liquid each time. One procedure is to allow the pipette to drain 1 min. after the bulk of the liquid has been delivered and then to touch the tip of the pipette to the side of the beaker, thereby removing the liquid which has accumulated over a definite draining time. A second procedure involves draining the pipette 15 sec. with the tip touching the side of the beaker after the main bulk of the liquid has been delivered. A third procedure is to allow the liquid to accumulate in the tip 15 sec. after the bulk has been delivered, then, by placing the index finger of the left hand over the top of the pipette and by firmly squeezing the bulb of the pipette with the right hand, the accumulated liquid is forced out. While all three procedures are entirely satisfactory, the second and third are slightly more rapid. Also, in the third procedure, the entire liquid accumulating in the tip is forced out and for this reason it is frequently preferred to the other methods. Blowing out the last quantity of the liquid by mouth should never be practiced.

*Calibration of Pipettes.* Insure that the pipette drains in the required time and that it drains clean. Obtain the weight of a glass-stoppered weighing bottle with a capacity somewhat greater than the volume delivered by the pipette. Fill the pipette to the mark with distilled water at room temperature, noting the temperature. Deliver the water into the weighing bottle, draining the pipette in the manner in which it is to be used thereafter. Weigh the water delivered to the nearest milligram. Calculate the actual volume of water delivered from the weight and the temperature of the water using Table 4. Duplicate determinations should agree within one one-thousandth, e.g., volumes delivered for a 10 ml. pipette should check to within 0.01 ml., for a 25 ml. pipette to within 0.03 ml., and for a 100 ml. pipette to within 0.1 ml.

**Tolerances for Volumetric Apparatus.** As in the case of analytical weights, the Bureau of Standards has established a list of tolerances for high-grade volumetric apparatus.

**Bureau of Standards Tolerances for Glass Volumetric Apparatus**[1]

*Flasks*

| Capacity (in ml.) less than and including | Limit of Error<br>If to contain (ml.) | Limit of Error<br>If to deliver (ml.) |
|---|---|---|
| 25 | .03 | .05 |
| 50 | .05 | .10 |
| 100 | .08 | .15 |
| 200 | .10 | .20 |
| 300 | .12 | .25 |
| 500 | .15 | .30 |
| 1,000 | .30 | .50 |
| 2,000 | .50 | 1.0 |
| 3,000 | .75 | 1.5 |
| 5,000 | 1.2 | 2.4 |

*Transfer Pipettes*

| Capacity (in ml.) less than and including | Limit of Error (ml.) |
|---|---|
| 2 | .006 |
| 5 | .01 |
| 10 | .02 |
| 30 | .03 |
| 50 | .05 |
| 100 | .08 |
| 200 | .10 |

The outlet of any transfer pipette must be of such a size that the free outflow shall last not more than 1 min. and not less than the following for the respective sizes:

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[1] U. S. Bur. of Standards, *Cir. No.* **C434** (1941).

| Capacity (in ml.) up to and including | Outflow Time (sec.) |
|---|---|
| 5 | 15 |
| 10 | 20 |
| 50 | 30 |
| 100 | 40 |
| 200 | 50 |

*Burettes*

| Capacity (in ml.) of total graduated portion less than and including | Limit of Error (ml.) |
|---|---|
| 5 | .01 |
| 10 | .02 |
| 30 | .03 |
| 50 | .05 |
| 100 | .10 |

### *Delivery Time*

The actual delivery time of any instrument must be within the limits prescribed in the specifications, and the error in the marked delivery time must not exceed the following:

| Delivery time (in sec.) less than and including | Limit of Error (sec.) |
|---|---|
| 15 | 3 |
| 20 | 4 |
| 30 | 6 |
| 50 | 8 |
| 100 | 15 |
| 200 | 20 |

## SOLUTIONS

Although the concentration of solutions may be expressed in several ways, there are two general types: percentage solutions and solutions prepared to contain a definite weight of solute per volume of solution. Included in this latter group are normal and molar solutions. The term standard solution is frequently used and refers to a solution whose concentration is known, irrespective of the manner in which the concentration is expressed.

**Percentage Solutions.** Percentage solutions may be either percentage by weight or percentage by volume solutions. Unless specifically designated as a percentage by volume solution, percentage solutions are considered as percentage by weight solutions.

A percentage by weight solution is based on the weight of solute in a definite weight of the solution. For example, to prepare a 10 per cent by weight sodium chloride solution, dissolve 10 grams of sodium chloride in 90 grams of water. The concentration of the solute in 1 ml. of the solution can be calculated for a certain temperature if the specific gravity at that temperature and the percentage strength are known.

A percentage by volume solution is based on the volumes of a pure solute per definite volume of solution. For example, a 10 per cent ethyl alcohol solution could be prepared by dissolving 10 ml. of absolute ethyl alcohol in sufficient water to give a total of 100 ml. of solution. Needless to say, percentage by volume solutions can only be prepared from liquids.

**Solutions Containing a Definite Weight of Solute per Volume.** A useful solution in analytical chemistry is one in which there is a known concentration of solute per volume of solution. For example, one may prepare a solution by dissolving 10 grams of sodium chloride in 100 ml. of solution. Every milliliter of solution will then contain 10/100 of the weight of solute or 0.1 gram of sodium chloride. At times this solution has been used incorrectly as a percentage solution. For dilute concentrations there is little difference between the two, however as the concentration increases, the difference becomes very large. Thus, 50 grams of sodium hydroxide dissolved in 100 ml. of solution gives a 36 per cent by weight solution and not a 50 per cent solution of sodium hydroxide.

Molar solutions also belong to this class since they contain a definite weight of solute per definite volume of solution. Molar solutions are prepared by dissolving a mole of the solute in 1000 ml. of solution.

**Normal Solutions.** Standard solutions in which the concentration is expressed in terms of reacting or chemical equivalents per unit of volume (solutions of definite normality) are used frequently in quantitative analysis. A normal solution is one which contains one gram equivalent of the active reagent per liter of solution. A normal solution of an acid contains 1.008 grams of available hydrogen ion per liter of solution, e.g., 1 mole of hydrochloric acid or one-half mole of sulfuric acid. A normal solution of a base contains in one liter enough available hydroxyl ion (17.008 grams) to combine with a normal weight (1.008 grams) of hydrogen ion. A normal solution of an oxidizing agent has an oxidizing value per liter of 8.000 grams of oxygen (1 gram atom of iodine or one-fifth mole of potassium permanganate in acid solution or one-third mole of potassium permanganate in alkaline solution). A normal solution of a reducing agent has a reducing value per liter of 1.008 grams of hydrogen (1 mole of ferrous sulfate or one-half mole of stannous chloride). A normal solution of a precipitating agent contains in a liter the weight of precipitating ion equivalent to 1.008 grams of hydrogen. The weight of a pure substance required for the preparation of a liter of a normal precipitating solution is obtained by dividing the gram-molecular weight by the valence of the precipitating ion. One milliliter of a normal solution is equivalent to one milliliter of any other normal solution.

A normal solution, by definition contains one equivalent weight of the material dissolved in a liter of solution. One milliliter of a normal solution, then, contains one one-thousandth of the equivalent weight, frequently designated as the milliequivalent weight. The milliequivalent weight is useful in those calculations involving the conversion of volumes to weight.

**Normal Factor.** The normal factor of a solution may be determined by titration against a standard solution of definite normality. In this way equivalent volumes of the two solutions are obtained, or, in other words, a volume ratio is established from which the normal factor may be calculated (see p. 294). The normal factor may also be obtained by titration of a definite weight of a pure substance, or primary standard (see p. 294). In a few instances, the normal factor is obtained from the weight of precipitate derived by the quantitative precipitation of an ion or radical of the solution, e.g., the precipitation of $Cl^-$ as AgCl from a hydrochloric acid solution or $SO_4^=$ as $BaSO_4$ from a sulfuric acid solution (see p. 294).

In general, normal solutions are too concentrated for use in volumetric procedures. Solutions containing a fraction of the equivalent or normal weight are most generally used. The strengths of these solutions may be expressed fractionally, for example, as N/2, N/5, or N/10 solutions, although the decimal expressions 0.5 N, 0.2 N, or 0.1 N, respectively, are preferable. Either the fractional or decimal expression of normality is called a "normal factor." The normal factor, then, expresses the concentration of a solution in terms of a normal solution.

At times, it is worth while to prepare solutions of exact normality (1 N, 0.1 N, etc.) to simplify future calculations. However, it is much easier and frequently just as satisfactory to prepare and use standard solutions which closely approximate these in value. In practice, the volume of such solutions can easily be converted to normal volume by multiplying by the normal factor. For example, 20.30 ml. of .1095 N solution are equivalent to 20.30 × .1095 or 2.22 ml. of a normal solution.

**Primary Standard.** A primary standard must be a substance which can be obtained in a pure state, weighed with a desirable accuracy, and titrated directly. The titration of a solution of unknown concentration against a primary standard is a direct and simple method for determining the normal factor of the solution. The choice of a particular primary standard for a standardization is largely a matter of personal preference and is determined mainly by the ease and speed with which the determination may be made.

The specifications of an ideal primary standard for the standardization of acids or bases are listed by Dodge.[1] These include:

1. The standard should be obtained easily in a pure state.
2. It should remain unaltered in the air, at ordinary or moderately high temperatures, that is, it should not be hygroscopic or efflorescent.
3. It should dissolve readily in water and alcohol, permitting immediate titration in the cold.
4. Its molecular or, more particularly, its equivalent weight should be high, thus decreasing the effect of small errors in weighing.
5. No interfering product should be formed upon titration.
6. It should be free from color, before and after titration, in order to avoid interference with indicators.

While no substance used as a primary standard may meet exactly all the specifications of an ideal standard, some approximate it rather closely. These are the primary standards which have been accepted and are in general use by analysts. A number of these substances may be secured from the manufacturers in a sufficiently pure state for use as primary standards, particularly if they are prepared and labeled for that purpose. However, the analyst may prefer to prepare and purify his primary standards from the manufactured products. Some of these methods will be discussed in connection with procedures for standardizing specific solutions. A few primary standards are available from the United States Bureau of Standards and, whenever possible, these standards are to be recommended.

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[1] Dodge, *Ind. Eng. Chem.*, **7**, 29 (1915).

TABLE 5. SOME PRIMARY STANDARDS FOR ACIDIMETRY AND ALKALIMETRY

| *Standards for Solutions of Acids* | *Standards for Solutions of Bases* |
|---|---|
| Sodium carbonate | Benzoic acid |
| Borax | Succinic acid |
| Calcium carbonate | Oxalic acid (crystalline) |
| Thallium carbonate | Sulfamic acid |
| Diphenyl guanidine | Constant boiling hydrochloric acid |
| Potassium iodate | Acid potassium phthalate |

# CHAPTER VI

# NEUTRALIZATION REACTIONS

Neutralization reactions are the basis for the methods involved in the determination of the total acidity or basicity of solutions. Fundamentally, neutralization reactions involve the interaction of $H^+$ and $OH^-$ with the formation of $H_2O$. Reactions of this type are used to measure the total amount of acid or base in a given solution, regardless of the degree of ionization involved. Sometimes, these values are designated as the titratable acidity or titratable alkalinity of a solution.

**H-ion Concentration and *p*H.** An acid is defined as a substance which will give H-ions as the only positive ions in solution. When an acid is dissolved in water some of the molecules dissociate into H-ions and acid-radical ions. If the concentration of H-ions in a 0.1 molar solution is high, the acid is said to be strong and, vice versa, if the concentration of H-ions is low, the acid is said to be weak. Such differences in the concentration of H-ions at a definite molarity are due to ionization of the acids. For purposes of clarification, molarity of solutions is specified, since even strong acids in extremely dilute solution would, of necessity, have very low H-ion concentrations.

It is essential to differentiate clearly between the quantity and the intensity factors of an acid. The quantity factor gives a measure of the total quantity of acid present (the titratable acidity), whereas the intensity factor gives a measure of the H-ion concentration. Although the actual concentration of free H-ion in a solution ($C_{H^+}$) may be relatively small at a particular instant, the total potential H-ion in a solution (titratable acidity) may be large. This is possible because ionization reactions are reversible reactions. This may be illustrated using acetic acid as an example:

$$\underset{\text{non-ionized}}{CH_3COOH} \rightleftarrows \underset{\text{ionized}}{CH_3COO^- + H^+}.$$

Acetic acid, except in extremely dilute solutions, is but slightly ionized, therefore its H-ion concentration at a particular moment is relatively low (a weak acid). However, in a neutralization reaction, as the H-ions react during titration with the OH-ions of a base, the reaction continues to the right because of the equilibrium relationship until the entire quantity of acetic acid has been neutralized.

Ionization reactions are reversible reactions. In the case of water some of the molecules ionize to give:

$$\underset{\text{non-ionized}}{H_2O} \rightleftarrows \underset{\text{ionized}}{H^+ + OH^-}$$

Water is said to be neutral because, when it ionizes, it gives an equal number of H-ions and OH-ions. If a substance capable of giving H-ions in solution is added to water, the aqueous solution will contain more H-ions than OH-ions and so the solution will have acidic properties.

In the case of pure water, when equilibrium is reached, the concentration of H-ions and OH-ions in equilibrium with the non-ionized $H_2O$ molecules has a definite value. This can be expressed by the equation:

$$\frac{C_{H^+} \times C_{OH^-}}{C_{HOH}} = K_{(\text{equil.})}.$$

Since water is considered a weak electrolyte and ionizes to only a slight extent into H-ions and OH-ions, the concentration of non-ionized water is extremely large in comparison to the concentration of the ions and, for all practical purposes, may be considered constant. This permits the simplification of the previous equation to:

$$C_{H^+} \times C_{OH^-} = K_{(\text{equil.})} \times C_{HOH} = K_w = 1 \times 10^{-14}.$$

in other words, the product of the concentration of the H- and OH-ions is a constant and at 25° C. has approximately the value $1 \times 10^{-14}$.

Pure water is 1/10,000,000 normal with respect to H-ions. The fraction 1/10,000,000 is more easily, and usually, expressed as $10^{-7}$ normal. Pure water may then be said to have an H-ion concentration of $10^{-7}$ normal. Since pure water has the same concentration of H-ions and OH-ions, the concentration of each must be $10^{-7}$ and $K_w$ is then $10^{-14}$, e.g.,

$$\begin{array}{cccc} \text{Concentration H-ion} & \times \text{ Concentration OH-ion} & = K_w \\ 10^{-7} & \times \qquad 10^{-7} & = 10^{-14}. \end{array}$$

The addition of an acid to water will increase the H-ion concentration of the solution. If, for example, enough hydrochloric acid were added to water to make a .0001 N hydrochloric acid solution, the H-ion concentration of the solution would be $10^{-4}$. The OH-ion concentration would then be $10^{-10}$ since the product of the concentration of H-ions and OH-ions must be $10^{-14}$.

The fact that the OH-ion concentration can be calculated easily if the H-ion concentration is known, makes it possible to express degrees of alkalinity in terms of H-ion concentration. Thus, at approximately 25° C., when the negative value of the exponent of 10 is 7, the solution is neutral, if less than 7 the solution is acidic and if more than 7 the solution is alkaline.

To simplify expressing H-ion concentration, particularly for the purpose of plotting graphs using logarithmic values, Sorensen has devised the term *p*H value, which is nothing more than the numerical value of the negative exponent of the H-ion concentration. The definition for *p*H is that it is the log of the reciprocal of the H-ion concentration. For example, if a solution has an H-ion concentration of $10^{-4}$ normal, its *p*H is 4. The *p*H scale, as ordinarily expressed, extends from 0 to 14, covering the range from approximately a 1-normal strong acid solution to a 1-normal strong base solution. However, negative *p*H values and values over 14 may obtain for concentrations above 1-normal. The *p*H scale from 0 to 14 covers a restricted range of concentrations, but it covers the range ordinarily encountered in agricultural and biological materials. It should also be emphasized that equal *p*H intervals do not represent equal changes in H-ion concentration, since the relation is exponential.

TABLE 6. CALCULATED *p*H, H- AND OH-ION CONCENTRATIONS FOR HYDROCHLORIC ACID AND SODIUM HYDROXIDE SOLUTIONS OF DEFINITE NORMALITIES AT APPROXIMATELY 25°C. AND ASSUMING COMPLETE IONIZATION

| Normality | Solution | $C_{H^+}$ | *p*H | $C_{OH^-}$ |
|---|---|---|---|---|
| 1.0 | N HCl | $1 \times 10^{-0}$ | 0 | $1 \times 10^{-14}$ |
| .1 | N HCl | $1 \times 10^{-1}$ | 1 | $1 \times 10^{-13}$ |
| .01 | N HCl | $1 \times 10^{-2}$ | 2 | $1 \times 10^{-12}$ |
| .001 | N HCl | $1 \times 10^{-3}$ | 3 | $1 \times 10^{-11}$ |
| .0001 | N HCl | $1 \times 10^{-4}$ | 4 | $1 \times 10^{-10}$ |
| .00001 | N HCl | $1 \times 10^{-5}$ | 5 | $1 \times 10^{-9}$ |
| .000001 | N HCl | $1 \times 10^{-6}$ | 6 | $1 \times 10^{-8}$ |
| Pure $H_2O$ | | $1 \times 10^{-7}$ | 7 | $1 \times 10^{-7}$ |
| .000001 | N NaOH | $1 \times 10^{-8}$ | 8 | $1 \times 10^{-6}$ |
| .00001 | N NaOH | $1 \times 10^{-9}$ | 9 | $1 \times 10^{-5}$ |
| .0001 | N NaOH | $1 \times 10^{-10}$ | 10 | $1 \times 10^{-4}$ |
| .001 | N NaOH | $1 \times 10^{-11}$ | 11 | $1 \times 10^{-3}$ |
| .01 | N NaOH | $1 \times 10^{-12}$ | 12 | $1 \times 10^{-2}$ |
| .1 | N NaOH | $1 \times 10^{-13}$ | 13 | $1 \times 10^{-1}$ |
| 1.0 | N NaOH | $1 \times 10^{-14}$ | 14 | $1 \times 10^{-0}$ |

The comparison of normalities of H-ion and OH-ion concentrations with corresponding *p*H values for solutions of various concentrations are given in Table 6.

**Indicators and End Point.** It is essential to know exactly when a reaction involved in a volumetric analysis or titration is completed. This is accomplished in most volumetric methods by an indicator, which, at the completion of the reaction, gives rise to a well-defined color change in the solution or the appearance of a precipitate. This is referred to as the end point of the titration.

The observed or practical end point of a titration is that point at which the indicator has changed color, denoting the completion of the main reaction. Actually, however, a slight excess of reagent has been added to react with the indicator causing the color change. In general, this slight excess must not exceed 1–2 drops of the reagent. Obviously, if the indicator is to be of any value in a quantitative volumetric analysis, it must give an observed end point which is as near as possible to the stoichiometrical end point of the reaction (when exact molecular quantities have reacted).

**Indicators for Neutralization Reactions.** Indicators commonly used to determine the end point of a neutralization reaction are complicated organic compounds. Each indicator is capable of existing in two different color forms—these two forms being interconvertible into one another at specific H-ion and OH-ion concen-

TABLE 7. THE COLOR OF SOME COMMON INDICATORS IN ACIDIC AND BASIC SOLUTIONS AND THE *p*H RANGE IN WHICH THEIR COLOR CHANGES

| Name | Color | | *p*H Range |
|---|---|---|---|
| | Acid | Base | |
| Thymol blue | Red | Yellow | 1.2–2.8 |
| Methyl orange | Red | Yellow | 2.9–4.0 |
| Congo red | Blue | Red | 3.0–5.0 |
| Sodium alizarin sulfonate | Yellow | Red | 4.0–6.0 |
| Methyl red | Red | Yellow | 4.2–6.3 |
| Cochineal | Yellow | Lilac | 4.7–6.2 |
| Bromocresol purple | Yellow | Purple | 5.2–6.8 |
| Bromothymol blue | Yellow | Blue | 6.0–7.6 |
| Litmus | Red | Blue | about 7 |
| Cresol red | Yellow | Red | 7.2–8.8 |
| Thymol blue | Yellow | Blue | 8.0–9.6 |
| Phenolphthalein | Colorless | Red | 8.3–10.0 |
| Thymolphthalein | Yellow | Blue | 9.3–10.5 |

trations. In general, the indicators do not change color at exact neutrality ($p$H 7). Table 7 illustrates, for a number of common indicators, the color changes they undergo and the $p$H range in which the color change occurs.

**Selection of the Proper Indicator.** The selection of the proper indicator for a neutralization reaction is very important. The following factors should be considered in the selection of the proper indicator:

1. The type of neutralization reaction, i.e., strong acid vs. strong base, weak acid vs. strong base, or strong acid vs. weak base.
2. The nature of the color changes and the ease with which these changes can be differentiated.

*Type of Neutralization Reaction.* In titrating a strong acid with a strong base, neutral (normal) salts are formed when the neutralization is complete. ~~Under these conditions~~, when the stoichiometrical point is reached a neutral solution ($p$H 7) should result, and an indicator changing at this $p$H should be an ideal one to use.

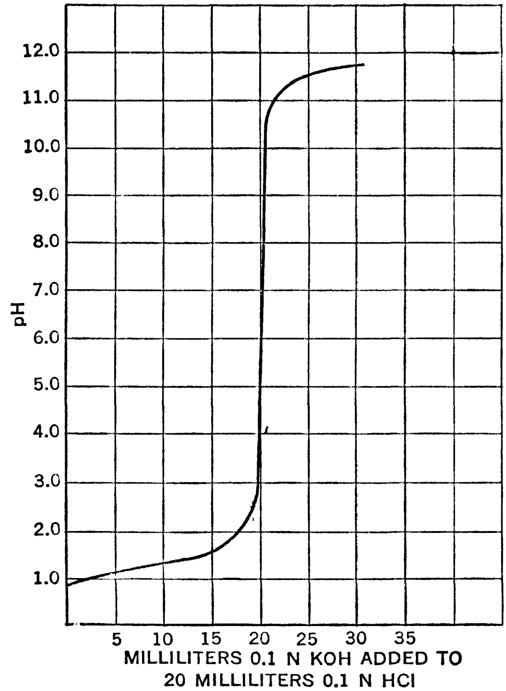

Fig. 13. Titration Curve for a Strong Acid vs. a Strong Base.

Actually, however, any of the indicators which change color between a *p*H of 4 and 9 will work satisfactorily. This is true because a few hundredths of a milliliter of tenth-normal acid or base will carry the H-ion or OH-ion concentration so far to either side of the neutral point that it will be within the range of color change of the indicator. This can best be illustrated in a neutralization (titration) curve for a strong acid titrated with a strong base, Fig. 13. It will be seen from the curve that the stoichiometrical end point compares favorably with the neutral point, and that the long vertical portion of the curve permits a wide change in *p*H with but very slight changes in the volumes of acid and base at the end point.

The most suitable indicator for the titration of a particular weak acid with a particular strong base, or vice versa, is determined by comparison of its range of color change with the *p*H of the stoichiometrically balanced salt solution. Thus, it should be emphasized that not all reactions involving a weak base and a strong acid or, vice versa, can be determined by the same indicators.

In titrating a weak acid (acetic acid) with a strong base (sodium hydroxide), the resulting solution at the stoichiometrical end point is alkaline in reaction due to the hydrolysis of the salt formed.

$$CH_3COOH + NaOH \rightleftarrows CH_3COONa + HOH.$$

An indicator, such as phenolphthalein, which changes color in an alkaline solution is suited for this type of titration. The neutralization curve for such a weak acid and strong base, Fig. 14, indicates that the stoichiometrical end point is above the neutral point (greater than *p*H 7) and well within the range of phenolphthalein.

In titrating a weak base (ammonium hydroxide) with a strong acid (hydrochloric acid), the resulting solution at the stoichiometrical end point is acid in reaction due to hydrolysis of the salt formed.

$$HCl + NH_4OH \rightleftarrows NH_4Cl + HOH.$$

An indicator, such as methyl orange, which changes color in an acid solution is best suited for this type of reaction. The neutralization curve for such a weak base and strong acid, Fig. 15, illustrates why methyl orange is the preferable indicator to use in this titration. The stoichiometrical end point is well below *p*H 7 and is comparable to the *p*H range at which methyl orange changes color.

The titration of a weak acid with a weak base should not be attempted.

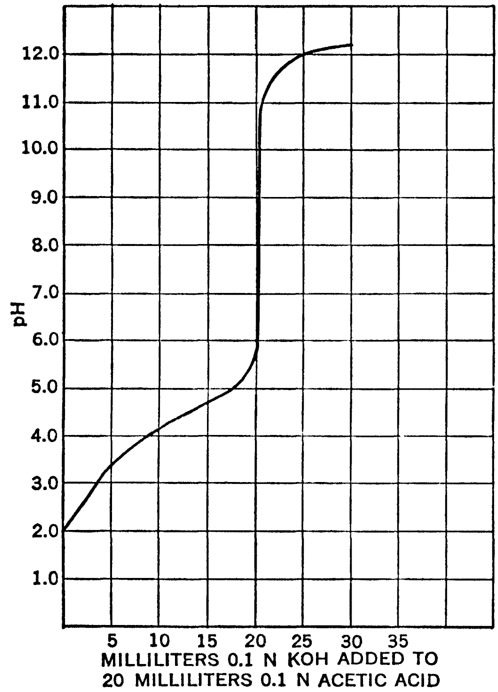

Fig. 14. Titration Curve for a Weak Acid vs. a Strong Base.

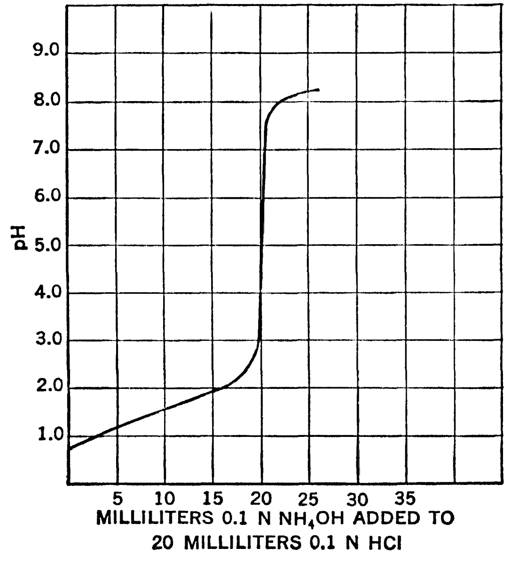

Fig. 15. Titration Curve for a Strong Acid vs. a Weak Base.

*Nature of Color Change and Ease of Detection.* The ease of detecting a color change of the indicator is an important factor in the selection of an indicator. A distinct change from colorless to red (e.g., phenolphthalein) is much easier to detect than a change from yellow to red through a range of orange color shades as in the case of methyl orange.

Mixed indicators consisting of indicator plus a dyestuff have an advantage in that they make possible a distinct color change usually from one hue to an entirely different hue. For example, in the titration of an acid with a base using methyl red as indicator, the acid solution is red. As neutralization by the base progresses, the solution becomes less and less red and more and more yellow until the color is distinctly yellow. In an identical titration but using a mixed indicator (methyl red and methylene blue) the color is purple in the acidic solution, and green in the basic solution with a gray transition point. The eye is capable of detecting this latter color change from purple to green through a neutral color (gray) much more readily than from red to yellow through a range in which there is a mixture of the two colors.

*Effect of Temperature.* The sensitivity of a given indicator may vary appreciably with temperature. Furthermore, an increase in temperature is likely to cause the indicator to begin to change color at a slightly lower *p*H. The shift is small and is different for each indicator. In general, when a solution has to be titrated at the boiling temperature, the standard solution should be standardized at that temperature using the same indicator.

**Preparation of Some Common Indicator Solutions for Acidimetry and Alkalimetry.**

*Bromthymol Blue:* Dissolve 0.1 gram of the indicator in 100 ml. of 50 per cent ethyl alcohol solution.

*Bromocresol Purple:* Grind together in an agate mortar, 0.100 gram of bromocresol purple with 9 ml. of 0.02 N sodium hydroxide solution. Dilute with water to 200 ml. and filter if necessary. The color of the solution should be a deep orange to red; if purple, the addition of not more than 0.5 ml. of 0.02 N acid should make it red; if yellow, the addition of not more than 0.5 ml. of 0.02 N sodium hydroxide solution should make it red.

*Cochineal:* Grind 1.0 gram of cochineal with 25 ml. of 95 per cent ethyl alcohol and 75 ml. of water. Allow to stand for 2 days and filter.

*Congo Red:* Dissolve 0.5 gram of congo red in 100 ml. of a 10 per cent ethyl alcohol solution.

*Cresol Red:* Dissolve 0.1 gram of the indicator in 100 ml. of 95 per cent ethyl alcohol solution.

*Methyl Orange:* Dissolve 0.1 gram of methyl orange in 100 ml. of hot water. After standing several hours filter if cloudy.

*Mixed Methyl Orange:* Dissolve 1.00 gram of methyl orange and 1.40 grams of xylene cyanole F.F. in a liter of water. The color change is from reddish purple in acid through a gray at *p*H near 4 to green in basic solution.

*Methyl Red:* Dissolve 0.2 gram of methyl red in 60 ml. of 95 per cent ethyl alcohol and dilute to 100 ml. with water.

*Mixed Methyl Red:* (a) Dissolve 1.250 grams of methyl red and 0.825 gram of methylene blue in one liter of 90 per cent ethyl alcohol. The color change is from purple in acid to green in basic solution. (b) Dissolve 0.75 gram of methyl red and 0.625 gram of guinea green in one liter of 90 per cent ethyl alcohol. The color change is from reddish-purple in acid to green in basic solution.

*Phenolphthalein:* Dissolve 1 gram of phenolphthalein in 50 ml. of 95 per cent ethyl alcohol and add 50 ml. of water.

*Sodium Alizarin Sulfonate:* Dissolve 0.25 gram of sodium alizarin sulfonate in 100 ml. of water and filter if cloudy.

*Mixed Sodium Alizarin Sulfonate:* (a) Dissolve 5.00 grams of sodium alizarin sulfonate and 0.625 gram of guinea green in one liter of water. The color change is from green in acid to violet-red in basic solution. (b) Dissolve 5.00 grams of sodium alizarin sulfonate and 1.25 grams of indigo carmine in one liter of water. The color change is from green in acid to red in basic solution.

*Thymol Blue:* Grind in an agate mortar, 0.10 gram of the dry indicator with 21.5 ml. of 0.01 N sodium hydroxide solution and dilute to 250 ml. with water.

*Thymolphthalein:* Dissolve 0.1 gram of the indicator in 200 ml. of 95 per cent ethyl alcohol solution.

## STANDARD SOLUTIONS OF ACIDS AND BASES: THEIR PREPARATION AND STANDARDIZATION

The ideal method for the preparation of an acidic or basic solution of definite normality would be to weigh the required quantity of the pure substance, dissolve it in water, and dilute to the proper volume. Unfortunately this cannot be done due to the fact that few substances are pure enough to be utilized in this manner. The usual method of preparation is to dissolve an approximate quantity of the substance in the proper volume and determine the exact normality of the resulting solution. The process of determining the normal factor of a solution is usually referred to as the standardization of the solution.

Pipettes, burettes and volumetric flasks used in volumetric procedures should be accurately calibrated and should meet the specifications established by the United States Bureau of Standards. Alkaline solutions are never kept in volumetric flasks since such solutions will dissolve glass and etch it. Burettes in which alkaline solutions are used should be recalibrated at definite periods of time.

The volume of a solution varies with temperature. Hence, a solution that is standardized at a certain temperature should be used at that temperature in order that its concentration will remain the same. This is especially true for solutions in which the solvent has a high coefficient of expansion. Temperature corrections for water solutions have been determined[1] and may be used with considerable accuracy.

**Preparation of an Approximately 0.1 N Sulfuric Acid Solution.** By definition, a normal solution of an acid contains one gram atom of replaceable H-ion per liter. Sulfuric acid with two replaceable H-ions per molecule will give twice the normal quantity of replaceable hydrogen if one mole of the acid is diluted to a liter. A normal solution of sulfuric acid will then require one-half mole of sulfuric acid per liter of solution, and a 0.1 N solution only one-tenth of the quantity required for a normal solution. The molecular weight of sulfuric acid is 98.1. One half the molecular weight is 49.1 and one-tenth of this is 4.9 grams—the quantity of sulfuric acid required to prepare one liter of 0.1 N solution.

Concentrated sulfuric acid is approximately 96 per cent pure and has a specific gravity of 1.84 (weight of one milliliter). On the assumption that these values are correct for the concentrated sulfuric acid available, one milliliter of concentrated sulfuric acid will then contain: $1.84 \times .96$ or 1.76 grams of pure sulfuric acid. As previously indicated, 4.9 grams of sulfuric acid are required to prepare one liter of 0.1 N solution. Since each milliliter of the concentrated acid was calculated to contain 1.76 grams of sulfuric acid, then $4.9 \div 1.76 = 2.78$, the number of milliliters of concentrated sulfuric acid required to give 4.9 grams of pure acid.

Since the specific gravity and percentage composition of the concentrated sulfuric acid used in the calculations were only approximations, the 2.78 ml. is also an approximation, and 3.0 ml. are usually used. Measure out 3.0 ml. of the concentrated sulfuric acid in a graduated pipette and dilute to one liter with water. After a thorough mixing, the solution is ready for standardization.

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[1] Kolthoff and Furman, "Volumetric Analysis," John Wiley & Sons, Inc., 2, 31 (1929).

**Standardization by Titration Against a Standard Alkali Solution.** If a standard solution of alkali is available, the sulfuric acid solution is readily standardized by direct titration against the standard alkali solution. From the volume ratio of the two solutions and the known normal factor of the alkali solution, the normal factor of the acid solution can be calculated.

Fill a burette with the standard alkali solution and another burette with the acid solution. Run exactly 20 ml. of the alkali solution into a 250 ml. beaker. Add 50 ml. of water and 2–3 drops of indicator solution (methyl red or mixed methyl red solution). Titrate to the end point with the acid solution, and calculate the volume ratio of the acid solution to the alkali solution. Add a measured volume (2–3 ml.) of the alkali solution to the beaker and again titrate to the end point with the acid solution. Calculate the volume ratio of the two solutions. Repeat the titrations until the volume ratios agree, then calculate the normal factor of the acid solution (see p. 294).

**Standardization by Titration Against a Primary Standard—Sodium Carbonate ($Na_2CO_3$).** Dry a shallow layer of analyzed C.P. grade sodium carbonate in a flat type weighing bottle for two hours or longer at 130°–150° C. Cover the dish and cool in a desiccator. Two methods for obtaining weighed samples for titration are available:

1. Weigh accurately, by difference, several samples of 0.1–0.2 gram each of the dried and cooled sodium carbonate into 400 ml. beakers and dissolve in 100 ml. of water.
2. Weigh accurately, by difference, a sample of 0.8–1.0 grams of the dried and cooled sodium carbonate into a 250 ml. volumetric flask. Dissolve in water and dilute to the mark. Carefully remove several 50 ml. aliquots to 400 ml. beakers by means of a calibrated 50 ml. bulb pipette, and dilute each to a volume of approximately 100 ml.

*Titration Using Methyl Orange as Indicator.* Add 2–3 drops of methyl orange or the mixed methyl orange indicator to the sample prepared by either of the above methods, and, with constant stirring, add the acid solution from a burette until the end point is reached. Carefully wash down the sides of the beaker with the wash bottle. If the solution changes color, add more acid until the end point is obtained.

*Titration Using Methyl Red as Indicator.* Since, for some analysts, the methyl orange end point is difficult to detect, other indicators may be used in such a titration with slight modifications. Add to the sample, prepared by either of the above methods, a measured quantity of the acid, insuring a definite excess (5–10 ml. excess acid). Boil this solution slowly for several minutes to expel all the carbonic acid produced in the reaction. Cool, and titrate to the end point with an alkali solution of approximately the same normality. The normality of the alkali solution need not be known, although it is necessary to know the volume ratio of the acid to alkali.

To illustrate:

35.00 ml. of acid solution added to insure an excess.
6.00 ml. of alkali solution used to titrate the excess acid.

The volume ratio of acid to alkali (determined independently): 1.00 ml. of acid solution is equivalent to 1.20 ml. of alkali solution.

Multiplying the milliliters of alkali used by the volume ratio: $6.00 \times \frac{1.0}{1.2} = 5.00$, the milliliters of acid equivalent to 6.0 ml. of alkali. In the reaction then, the 6.00 ml. of alkali neutralized 5.00 ml. of the acid. Subtracting this quantity of acid (the excess) from the total amount used: 35.00 ml. − 5.00 ml. = 30.00 ml., the milliliters of acid actually used to neutralize the sodium carbonate sample.

From the weight of sodium carbonate sample and the milliliters of acid required to neutralize it, calculate the normal factor of the acid solution (see p. 294). Replicate normal factors should check within 5 in the fourth decimal place to be acceptable.

**Standardization by Titration Against a Primary Standard—Borax ($Na_2B_4O_7 \cdot 10\,H_2O$).** Borax used as a primary standard in acidimetry, as suggested by Hurley,[1, 2] has proved very satisfactory. The main objection to the use of borax as a primary standard has been that it is hydrated and so is susceptible to changes in composition through variation in its water content. Simple procedures for the preparation and preservation of the decahydrate have overcome this objection to a large extent.

*Preparation and Preservation of Borax.* The pure decahydrate is obtained by dissolving 15 grams of analyzed C.P. grade borax in 50 ml. of water with heating. On cooling, the pure decahydrate

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[1] Hurley, *Ind. Eng. Chem., Anal. Ed.*, 8, 220 (1936).

[2] Hurley, *Ind. Eng. Chem., Anal. Ed.*, 9, 237 (1937).

crystallizes out below 55° C. and is separated from the mother liquor by filtering through a filter paper in a Buechner funnel using suction, then washed twice with water. The crystals are dried by washing twice with 5 ml. portions of ethyl alcohol for every 10 grams of crystals, then twice with 5 ml. portions of ethyl ether using suction after the addition of each wash solution. Spread the crystals in a thin layer on a watch glass at room temperature until the ether evaporates and the crystals are dry.

The dry crystals may be kept for a considerable period of time by storage in a tightly closed container.[1] For longer periods, the crystals will retain their proper moisture content if stored in a desiccator over a solution saturated with respect to both sucrose and sodium chloride.

*Titration.* Dissolve accurately weighed samples of approximately 0.5 gram of the prepared dry borate crystals in 25 ml. of water, add 5 drops of methyl red or mixed methyl red indicator and titrate to the end point. From the weight of sample and the milliliters of acid required to neutralize it, calculate the normal factor of the acid solution. Due to the relatively high equivalent weight of borax (190.71), which permits weighing out a large sample for titration, any error in weighing is minimized and replicate normal factors should agree closely.

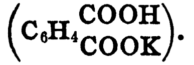
**Standardization by the Barium Sulfate Precipitation Method.** Dilute 25.00 ml. of the acid to be standardized to approximately 100 ml.; heat to boiling and add, dropwise, a 10 per cent barium chloride solution until no further precipitation occurs. Continue the boiling for about 5 min., allow to stand for 5 hours or longer in a warm place. Pour the supernatant liquid on a weighed Gooch crucible or an ashless filter. Treat the precipitate with 25–30 ml. of boiling water, transfer to the filter and wash with boiling water until the filtrate is free from chlorides. Dry, ignite and weigh as barium sulfate. From the weight of barium sulfate obtained, calculate the normal factor of the sulfuric acid solution.

**Preparation of an Approximately 0.1 N Sodium Hydroxide Solution.** A normal solution of an alkali contains one gram atom of replaceable OH-ion (17.008 grams) per liter of solution. This quantity of OH-ion is contained in one mole of sodium hydroxide (40.005 grams). One liter of a normal sodium hydroxide solution will then contain 40.005 grams of sodium hydroxide and a liter of 0.1 N solution will contain one-tenth as much, or 4.0005 grams. Since the commercial stick or pellet sodium hydroxide is always contaminated with carbonate, about 4.5–5.0 grams of sodium hydroxide should be dissolved and diluted to a liter for an approximately 0.1 N solution. The solution must be kept in a rubber-stoppered bottle and never in a glass-stoppered bottle since alkali will cement (freeze) the glass stopper to the bottle.

Since solid sodium hydroxide is always contaminated by carbonate and is also difficult to weigh, a saturated solution of sodium hydroxide is frequently employed for the preparation of an approximately 0.1 N solution. Carbonates are not soluble and precipitate out in a saturated sodium hydroxide solution so that a carbonate-free solution is obtained. Furthermore, once the concentration of the saturated solution at room temperature has been determined, measured volumes of it may easily be utilized in the preparation of standard solutions of weaker concentration.

A saturated sodium hydroxide solution is about a 50.1 per cent solution with a specific gravity of 1.53. A milliliter of the saturated solution will thus contain 1.53 gram × .501 or .7665 gram of sodium hydroxide. A liter of 0.1 N sodium hydroxide should contain 4.0 grams of sodium hydroxide. Then, since every milliliter of saturated sodium hydroxide contains .7665 gram of sodium hydroxide, $4.0 \div .7665 = 5.2$, the number of milliliters of saturated sodium hydroxide which will contain 4.0 grams of sodium hydroxide, and which, when diluted to 1 liter will make an approximately 0.1 N solution. To prepare a liter of approximately 0.1 N sodium hydroxide solution, dilute 5.2 ml. of the saturated sodium hydroxide to a liter with carbon dioxide-free water.

**Standardization by Titration Against a Standard Acid.** To a measured volume of an acid solution of known normality, add 2–3 drops of an indicator solution, dilute to a volume of approximately 50 ml., and titrate with the alkali solution to be standardized. At the end point of the titration, the milliliters of acid solution multiplied by their normal factor will be equivalent to the milliliters of alkali solution multiplied by their normal factor. From this statement, calculate the normal factor of the alkali solution (see p. 294).

**Standardization by Titration Against a Primary Standard—Acid Potassium Phthalate**  $\left(\mathrm{C_6H_4}{}^{\mathrm{COOH}}_{\mathrm{COOK}}\right)$. Acid potassium phthalate has a relatively high equivalent weight (204.2). Since it contains only one acid or replaceable hydrogen, its molecular weight is its equivalent weight. It is readily obtained in a pure state and is not appreciably affected by the atmosphere. Acid potassium phthalate for use as a primary standard may be obtained from the United States Bureau of Standards.

*Preparation of the Acid Potassium Phthalate Solution for Titration.* Dry a shallow layer of the pure acid potassium phthalate in a flat type weighing bottle for two hours or longer at 110°–120° C. and cool in a desiccator. Weigh accurately about 0.5 gram samples of the dried standard into 300 ml. Erlenmeyer flasks and dissolve each sample in 50 ml. of carbon dioxide-free water (recently boiled and cooled). An alternate procedure is to weigh exactly 2.500 grams of the dried acid potassium phthalate, transfer it to a 250 ml. volumetric flask, dissolve in carbon dioxide-free water and dilute to the mark. Remove, by means of a 50 ml. calibrated bulb pipette, 50.00 ml. aliquots of the solution into 300 ml. Erlenmeyer flasks.

*Titration.* Titrate the acid potassium phthalate solution prepared by either method with the sodium hydroxide solution to be standardized, using phenolphthalein as indicator. The first noticeable persistent pink coloration is taken as the end point, and replicate determinations should agree closely. Since a weak acid is being titrated by a strong base, an indicator which changes color above *p*H 7 is required, hence the use of phenolphthalein with the attendant precautions to eliminate carbon dioxide.

**Standardization by Titration Against a Primary Standard—Benzoic Acid ($C_6H_5COOH$).** Benzoic acid has a fairly high equivalent weight (122.1) and may be obtained readily in a pure form. Samples for use as a primary standard may be obtained from the United States Bureau of Standards. Benzoic acid is not soluble in cold water and so must be dissolved in alcohol. It is a weak acid and so phenolphthalein is required as an indicator in the titration.

*Preparation of the Benzoic Acid Solution for Titration.* Benzoic acid may be purified by recrystallization from water and also by sublimation. If a high degree of accuracy is desired, the acid should also be fused. This is accomplished by heating the benzoic acid contained in glass or platinum dishes in an air bath at a temperature not to exceed 130°–135° C. Heating should be stopped as soon as the fusion is complete.

Weigh accurately samples of 0.3–0.4 gram of the pure benzoic acid and transfer to 400 ml. beakers. Dissolve each sample in 25 ml. of ethyl alcohol.

*Titration.* To the alcohol solution of the benzoic acid add 2–3 drops of phenolphthalein indicator and titrate to the first noticeable persistent pink coloration. The titration must be made in the cold.

A blank titration must be made on the same volume of alcohol as was used to dissolve each benzoic acid sample. The value obtained in this blank determination is subtracted from the titration figures on the samples to correct them for the amount of alkali solution required to give the alcohol a noticeable pink coloration in the presence of phenolphthalein.

From the weight of sample titrated and the corrected titration figure, calculate the normal factor of the alkali solution. Replicate values should check closely.

**Standardization by Titration Against a Primary Standard—Sulfamic Acid ($NH_2SO_3H$).** Sulfamic acid[1] is a crystalline non-hygroscopic solid readily obtained in a pure form or easily purified by recrystallization from water and drying in air. It is a strong acid in aqueous solution and can be titrated with alkali solutions using indicators which change color from *p*H 4–9. This gives it an advantage over the other standards for basic solutions since they are weak acids and so require phenolphthalein as an indicator. Its equivalent weight (97.09) is relatively low in comparison with a standard such as acid potassium phthalate.

*Preparation of the Sulfamic Acid Solution for Titration.* Accurately weigh 2.4273 grams of the pure crystalline sulfamic acid and transfer to a 250 ml. volumetric flask. Dissolve in water and dilute to the mark. The resulting solution is an exactly 0.1000 N solution of the acid.

*Titration.* Remove, by means of a calibrated bulb pipette, 25 ml. aliquots of the solution to 400 ml. beakers. Add several drops of an indicator solution (any of the common indicators which change color in the *p*H range 4–9 may be used) and titrate to the end point with the alkali solution to be standardized. Calculate the normal factor of the alkali solution.

**Preparation of a Standard Solution of Exact Normality.** At times it is desirable to prepare a considerable quantity of standard solution of definite normality. This may be accomplished by diluting a more concentrated solution[2] or by adding a more concentrated solution to a weaker solution until the desired normality is obtained. Hydrochloric acid solutions of exact normality may be prepared by diluting weighed portions of "constant boiling" hydrochloric acid to the proper volume.[3]

## ANALYSIS OF A COMMERCIAL SODA ASH

Commercial soda ash (sodium carbonate) may contain as impurities sodium hydroxide or sodium bicarbonate. By a titration involving two indicators (phenolphthalein and methyl orange) the amounts of sodium carbonate, sodium bicarbonate, and sodium hydroxide may be determined. This determination depends upon the color change of indicators at different H-ion concentrations or *p*H's.

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[1] Butler, Smith, and Audrieth, *Ind. Eng. Chem., Anal. Ed.*, **10**, 690 (1938).

[2] Johnson, *Ind. Eng. Chem., Anal. Ed.*, **7**, 76 (1935).

[3] Hulett and Bonner, *J. Amer. Chem. Soc.*, **31**, 390 (1909).

The neutralization of a mixture of sodium hydroxide and sodium carbonate by an acid, using phenolphthalein as an indicator, goes through the following stages. The acid first neutralizes the base, then converts the sodium carbonate to sodium bicarbonate:

$$NaOH + HCl \rightarrow NaCl + H_2O$$
$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl.$$

Further addition of acid after the above reactions are complete produces carbonic acid. A sodium bicarbonate solution has a *p*H on the acid side of the range for phenolphthalein, so the solution is colorless.

In the case of a solution of sodium carbonate and sodium bicarbonate, the addition of acid will cause the sodium carbonate to be converted to bicarbonate and, when the conversion is complete, the red color of phenolphthalein will disappear.

In either of the above situations, if methyl orange indicator is added after the decolorization of the phenolphthalein, the bicarbonate may be titrated by the acid:

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2.$$

The *p*H of the solution due to the ionized sodium bicarbonate and liberated carbonic acid is greater than that at which methyl orange changes color; therefore it has no effect upon the indicator. When all the sodium bicarbonate has reacted with the acid, the next drop of strong acid will lower the *p*H of the solution to the point where the methyl orange changes color.

The quantity of acid used to titrate with phenolphthalein represents the total amount of sodium hydroxide and one half of the amount of sodium carbonate. That used with the methyl orange represents the other half of the amount of sodium carbonate and any sodium bicarbonate which may have been originally present as such.

In the event that the sample contained sodium carbonate and sodium bicarbonate, the volume of acid used with phenolphthalein will be less than that used with methyl orange as indicator. A sample of sodium hydroxide and sodium carbonate would require a larger volume of acid with phenolphthalein than with methyl orange as indicator.

*Procedure.* Dry the sample for 4 hours at 100° C. and cool in a desiccator. Samples of soda ash absorb water readily and so every precaution must be taken to keep the dried sample out of contact with the air. Carefully weigh, by difference, two samples of about 0.2 gram in size into two 300 ml. Erlenmeyer flasks. Dissolve in 100 ml. of water and add 3–4 drops of phenolphthalein indicator. Place the flask and sample in an ice-water bath and titrate with standard 0.1 N sulfuric acid to the decolorization of the solution. Record the volume of acid used in your notebook. Remove the flask from the ice-water bath and add 5–6 drops of methyl orange indicator. Continue the titration with the acid to the methyl orange end point and record in your notebook. From these results, ascertain what constituents were present in the sample and the percentage of each in the mixture.

The quantitative conversion of carbonate to bicarbonate takes place only at 0° C.; hence the use of the ice-water bath in the titration using phenolphthalein.

## VINEGAR

Vinegar is produced by the successive alcoholic and acetic fermentations of a fruit or sugar solution by certain yeasts and bacteria. The most important constituent of vinegar is acetic acid. The minimum percentage of acetic acid in vinegar is regulated by Federal and State Food Laws. The Federal Food and Drug Administration (1936) stated that "cider or apple vinegar should contain in 100 ml. (20° C.) not less than 4 grams of acetic acid."

**Determination of the Acidity of Vinegar.** A measured volume of the vinegar is titrated with standard 0.1 N alkali solution using phenolphthalein as an indicator. From the volume of the standard alkali used, calculate the acidity as grams of acetic acid per 100 ml. of vinegar.

*Procedure.* With the aid of a 5 ml. bulb pipette, carefully transfer 5.00 ml. of the vinegar sample into a 300 ml. Erlenmeyer flask. If a clean dry pipette is not available, rinse a wet pipette several times with the vinegar, discarding the rinsings.

Dilute the sample with 50 ml. of recently boiled but cold distilled water. Add a few drops of phenolphthalein indicator and titrate with the standard 0.1 N alkali solution until the first permanent pink color is detected. Repeat the determination with another 5.00 ml. portion of the vinegar. Duplicate determinations should check within 0.1 ml. From the volume of standard alkali used, calculate the grams of acetic acid present in 100 ml. of the vinegar.

*Remarks.* Water is added to the sample to dilute the dark color of some vinegars and thus make the indicator color change more easily detected. Since phenolphthalein is used as an indicator, the solution must be carbon dioxide-free, hence the necessity for using recently boiled distilled water. The solution is kept cold to decrease the volatility of the acetic acid.

## CHAPTER VII

## OXIDATION AND REDUCTION REACTIONS

Numerous volumetric methods are based upon oxidation-reduction reactions. These reactions involve valence changes (electron transfers) and, in this respect, differ appreciably from the neutralization and precipitation volumetric methods. Because of this difference, it is important to consider briefly the fundamentals of oxidation-reduction reactions.

The simplest conception of an oxidation reaction is the direct addition of oxygen, e.g., $2\ H_2 + O_2 \rightarrow 2\ H_2O$. In this case the hydrogen has been oxidized and the oxygen reduced to form water.

It is not necessary, however, to involve oxygen in an oxidation reaction. For example, in the following reaction: $2\ H_2S + SO_2 \rightarrow 2\ H_2O + 3\ S$, the $H_2S$ is oxidized and the $SO_2$ reduced. The removal of hydrogen, or its equivalent, from a compound as well as the addition of oxygen or its equivalent is considered an oxidation. In a similar manner, the removal of oxygen from or the addition of hydrogen to a compound can be considered a reduction.

Still another conception of oxidation and reduction is in terms of valence change and electron transfer. This concept has been especially valuable in considering oxidation-reduction reactions involving electrolytes in water solution. Let us consider, for example, the reaction between ferrous chloride and chlorine in solution:

$$2\ FeCl_2 + Cl_2 \rightarrow 2\ FeCl_3.$$

Since most salts in fairly dilute solution are, for all practical purposes, completely ionized, the reaction may be written in ionic form:

$$2\ Fe^{++} + 4\ Cl^- + Cl_2 \rightarrow 2\ Fe^{+++} + 6\ Cl^-.$$

In this reaction, the iron is oxidized and the molecular chlorine reduced. The iron has increased from a positive charge of +2 to +3, whereas the neutral chlorine molecule has been changed to negatively charged chloride ions. Oxidation, then, is a gain in positive charge and reduction a gain in negative charge or decrease in positive charge.

A gain in positive charge by an atom, radical, or ion is the result of a loss of one or more electrons. Conversely, a decrease in positive charge (gain in negative charge) results from the gain of one or more electrons. We may then state that oxidation means the loss of one or more electrons and reduction the gain of one or more electrons.

The loss or gain of electrons by an atom is associated with its valence. When ferrous iron ($Fe^{++}$) in the above reaction is oxidized to ferric iron ($Fe^{+++}$) it has lost an electron and its valence has changed from +2 to +3. The neutral chlorine has gained electrons so that each atom of chlorine has a valence of −1. Oxidation may then be considered as a gain in positive valence and reduction a decrease in positive valence or gain in negative valence.

**Balancing Oxidation-Reduction Equations by Valence Change.** In writing and balancing oxidation-reduction equations, it is essential to know the substances involved in the reaction and the products formed. Such information may be obtained from textbooks or by experiment. The next step involves writing the equation in an unbalanced molecular form. Taking, as an example, the oxidation of ferrous sulfate by potassium permanganate in acid solution, the unbalanced equation would be:

$$FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + MnSO_4 + K_2SO_4 + H_2O.$$

The ionic equation for the ions concerned in the oxidation-reduction would be:

$$Fe^{++} + \left[Mn^{\overset{++++}{+++}}O_4^{=}\right]^{-} + H^{+} \rightarrow Fe^{+++} + Mn^{++} + H_2O.$$

The manganese atom in the permanganate ion has a valence of +7, while in the manganous state it has a valence of +2. Thus each manganese atom suffers a reduction of five positive valencies. The five positive charges lost on the permanganate ion must be accounted for by a gain in positive charge on the iron. Since each ferrous ion shows an increase of one positive valence (charge) on becoming a ferric ion, the five positive charges from the permanganate ions are assumed by 5 ferrous ions. Since there are four atoms of oxygen involved, eight atoms of hydrogen are required to form four molecules of water. The left part of the equation calculated so far would be:

$$5\,FeSO_4 + KMnO_4 + 4\,H_2SO_4 \rightarrow$$

However, by inspection, it is seen that at least two $KMnO_4$ will be required so that one molecule of $K_2SO_4$ may be formed. This necessitates multiplying all coefficients by two. When this is done we get:

$$10\,\mathrm{FeSO_4} + 2\,\mathrm{KMnO_4} + 8\,\mathrm{H_2SO_4} \rightarrow 5\,\mathrm{Fe_2(SO_4)_3} + 2\,\mathrm{MnSO_4} + \mathrm{K_2SO_4} + 8\,\mathrm{H_2O}.$$

**Balancing Oxidation-Reduction Equations by Electron Transfers.** Here again it is necessary to know the substances involved in the reaction and the products formed. Then, considering the electronic changes involved, it is relatively simple to write and balance the equation. Oxidizing agents take up electrons; reducing agents lose electrons. Therefore, the equation must contain the correct number of ions or atoms of each substance so that the number of electrons furnished by the reducing agent is equivalent to the number of electrons taken up by the oxidizing agent. When this has been accomplished, it is simply necessary to see that the reactants on the left-hand side of the equation contain the correct number of atoms of each substance to correspond with the number of atoms on the right-hand side.

Again considering the oxidation of ferrous sulfate by potassium permanganate:

$$\begin{array}{l}[\mathrm{Mn}^{+7}\quad \mathrm{O}_4^{-2}]^{-1} \;+\; \mathrm{Fe}^{+2} \rightarrow \mathrm{Mn}^{+2} \;+\; \mathrm{Fe}^{+3}.\\ \qquad\qquad\qquad +\,5\,\epsilon \\ \qquad\qquad\qquad\qquad\qquad -\,1\,\epsilon\end{array}$$

The electrons gained by the manganese atom are lost by the ferrous ions in being oxidized to the ferric state. Since five electrons are gained by the manganese atom, five electrons must be lost by the iron, which necessitates multiplying each iron atom by five:

$$[\mathrm{Mn}^{+7}\quad \mathrm{O}_4^{-2}]^{-1} \;+\; 5\,\mathrm{Fe}^{+2} \rightarrow \mathrm{Mn}^{+2} \;+\; 5\,\mathrm{Fe}^{+3}.$$

On completing the equation with the other atoms involved, but which do not undergo electron transfers, it is noted that two molecules of potassium permanganate will be required to produce one molecule of potassium sulfate. This requires multiplying all coefficients by two, and when this is done the partially balanced equation is:

$$2\,\mathrm{KMnO_4} + 10\,\mathrm{FeSO_4} + \mathrm{H_2SO_4} \rightarrow 5\,\mathrm{Fe_2(SO_4)_3} + 2\,\mathrm{MnSO_4} + \mathrm{K_2SO_4} + \mathrm{H_2O}.$$

Eighteen $\mathrm{SO_4}$ radicals are present on the right-hand side of the equation so that eight $\mathrm{H_2SO_4}$ molecules must be required on the left side of the equation. The eight atoms of oxygen will react with the sixteen atoms of hydrogen on the left-hand side of the equation to give eight molecules of water. The balanced equation resulting from this is:

$$2\ KMnO_4 + 10\ FeSO_4 + 8\ H_2SO_4 \rightarrow 5\ Fe_2(SO_4)_3 + 2\ MnSO_4 + K_2SO_4 + 8\ H_2O.$$

## PERMANGANATE METHODS

Potassium permanganate is perhaps the most extensively used oxidizing agent in volumetric procedures because of its strong oxidizing ability and the fact that it functions as its own indicator, in that a slight excess of permanganate gives to a solution a definite pink color. As slight disadvantages may be mentioned the intense color of the permanganate solution which makes accurate burette readings difficult and the instability of its solutions unless properly prepared and protected from all reducing materials and light.

Permanganate reacts quantitatively with a great number of reducing substances in acid solution and with some substances in neutral or alkaline solution. Sulfuric and perchloric acids are not affected by permanganate and so are most commonly used to create an acid medium for the titration. Hydrochloric acid may be used if the titration is carried out in the cold and in dilute solution. Under these conditions, the chloride ion is not rapidly oxidized by the permanganate. However, in certain titrations, the constituent being determined induces a reaction between permanganate and chloride ion and thus renders the use of hydrochloric acid objectionable. Nitric acid, being an oxidizing agent, cannot be used to create an acid medium for permanganate titrations. In acid solution, the $MnO_4^-$ ion is reduced to the divalent $Mn^{++}$ ion whereas in neutral or alkaline solution, the $MnO_4^-$ ion is reduced to the tetravalent state and precipitated as $MnO_2$.

**Application of Permanganate Methods.** Many substances present in the reduced state may be titrated directly by a standard permanganate solution in an acid medium. This procedure is used frequently for the volumetric determination of iron, free oxalic acid, soluble oxalates, nitrites, and hydrogen peroxide. Reactions between permanganate and these reducing substances are:

$$2\ KMnO_4 + 10\ FeSO_4 + 8\ H_2SO_4 \rightarrow 5\ Fe_2(SO_4)_3 + 2\ MnSO_4 + K_2SO_4 + 8\ H_2O$$

$$2\ KMnO_4 + 5\ H_2C_2O_4 + 3\ H_2SO_4 \rightarrow K_2SO_4 + 2\ MnSO_4 + 10\ CO_2 + 8\ H_2O$$

$$2\ \mathrm{KMnO_4} + 5\ \mathrm{HNO_2} + 3\ \mathrm{H_2SO_4} \rightarrow 5\ \mathrm{HNO_3} + 2\ \mathrm{MnSO_4} + \mathrm{K_2SO_4} + 3\ \mathrm{H_2O}$$

$$2\ \mathrm{KMnO_4} + 5\ \mathrm{H_2O_2} + 4\ \mathrm{H_2SO_4} \rightarrow 5\ \mathrm{O_2} + 2\ \mathrm{MnSO_4} + 2\ \mathrm{KHSO_4} + 8\ \mathrm{H_2O}.$$

In certain methods, a measured excess of standard reducing substance is added and the standard permanganate solution is used to determine the unused excess of standard reducing solution in an acid medium. This is illustrated in determining the percentage purity of a manganese dioxide ore, pyrolusite. Here a measured excess of standard ferrous sulfate solution is added to an acid solution of the ore. The $MnO_2$ is reduced to the manganous form and an equivalent amount of the ferrous ion is oxidized to the ferric state. At the completion of the reaction, the unused ferrous ion is quantitatively oxidized by the standard permanganate solution.

A number of metallic ions may be quantitatively precipitated from solution as insoluble oxalates and determined volumetrically by dissolving in sulfuric acid and titrating the liberated oxalic acid with standard permanganate solution. This method is used extensively for the determination of calcium and a laboratory exercise is given for this determination. Other metallic ions which may be determined in this same manner are strontium, barium, lead, copper, and zinc.

Manganous salts may be oxidized by permanganate solution in neutral or alkaline medium. This is an interesting reaction in that one compound of manganese ($MnSO_4$) reacts with another ($KMnO_4$) to form a third compound of manganese ($MnO_2$). The reaction involved is:

$$2\ \mathrm{KMnO_4} + 3\ \mathrm{MnSO_4} + 2\ \mathrm{H_2O} \rightarrow 5\ \mathrm{MnO_2} + \mathrm{K_2SO_4} + 2\ \mathrm{H_2SO_4}.$$

In this reaction, the manganese in the $MnO_4^-$ ion goes from a valence of +7 to a valence of +4 in the $MnO_2$. Consequently the equivalent weight of potassium permanganate when used in neutral or alkaline medium is its molecular weight divided by three.

**Preparation of an Approximately 0.1 N Potassium Permanganate Solution for Use in an Acid Medium.** A normal solution contains one gram—equivalent weight of the oxidizing agent per liter (8.0000 grams oxygen) and corresponds to one unit change in valence. In acid solution for $KMnO_4$ we have:

$$\left[\mathrm{Mn}^{\overset{++++}{+++}}\mathrm{O}_4^{=}\right]^{-} \rightarrow \mathrm{Mn}^{++}.$$

This represents a change in valence from +7 to +2, or a net decrease of five positive charges per manganese atom. Thus a normal solution would contain one-fifth of a mole of potassium permanganate or 31.61 grams and a 0.1 N solution, 3.161 grams per liter of solution.

Dissolve 3.25 grams of potassium permanganate in a liter of water and boil for several minutes. Allow the solution to stand for several days, then heat to boiling and filter through a carefully prepared asbestos filter using suction. Store in a brown glass bottle with a glass stopper. The filtering removes hydrated $MnO_2$, which, if allowed to remain in the solution, would cause the solution to decrease in strength. The solution should be kept away from strong light by storing in a dark glass bottle and every effort should be made to keep the solution out of contact with dust and organic matter.

**Standardization by Titration Against a Primary Standard—Sodium Oxalate ($Na_2C_2O_4$).** This standard is the one most commonly used for the standardization of potassium permanganate solutions. It can be obtained readily in a pure form and is not appreciably hygroscopic. Sodium oxalate in a highly purified form for use as a primary standard may be obtained from the United States Bureau of Standards. The reactions involved when sodium oxalate is titrated with potassium permanganate are:

$$5\,Na_2C_2O_4 + 5\,H_2SO_4 \rightarrow 5\,Na_2SO_4 + 5\,H_2C_2O_4$$

$$5\,H_2C_2O_4 + 3\,H_2SO_4 + 2\,KMnO_4 \rightarrow K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O.$$

Since five moles of sodium oxalate react with ten equivalent weights of potassium permanganate, one equivalent weight of potassium permanganate will react with one-half mole of sodium oxalate. The equivalent weight of sodium oxalate would thus be $\frac{Na_2C_2O_4}{2}$ or $\frac{134.01}{2}$ or 67.00 grams and the milliequivalent weight would be 0.0670 gram.

Dry a shallow layer of the pure sodium oxalate in a flat type weighing bottle for one hour or longer at 100°–110° C. Cover the dish and cool in a desiccator.

Weigh accurately, by difference, several samples of 0.25–0.30 gram each of the dry sodium oxalate into 400 ml. beakers. Dissolve each portion in 200 ml. of water and heat to 80°–90° C. Remove from the flame, add 10 ml. of dilute sulfuric acid (1 volume concentrated acid:1 volume of water), and titrate this solution at once with the potassium permanganate solution to be standardized, stirring vigorously throughout the titration using a thermometer for a stirring rod. Add the permanganate solution slowly at first and then more rapidly as the titration progresses until near the end point, where the addition should again be made more slowly. The end point of the titration is taken as the first pink coloration which persists for 30 sec. due to a slight excess of the permanganate solution after all the sodium oxalate has reacted. If, during the titration, the temperature of the solution should drop below 65° C., the solution should again be heated to 80°–90° C. before completing the titration. The oxidation is catalyzed by manganous salts and so the reaction proceeds slowly at the start. The reaction is slow in a cold solution, hence the necessity for heating.

Calculate the normal factor of the potassium permanganate solution from the volumes of potassium permanganate required to react with each of the weighed samples of sodium oxalate. Replicate normal factors should agree within five ten-thousandths.

✓**The Determination of Calcium (in the Absence of Appreciable Quantities of Magnesium).** Calcium is determined volumetrically by first precipitating it as insoluble calcium oxalate, which is then filtered, washed and titrated with standard potassium permanganate solution in an acid medium. Assuming the calcium to be in the form of calcium carbonate, the reactions involved are:

For solution—

$$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + CO_2 + H_2O.$$

For precipitation (in excess ammonium hydroxide)—

$$CaCl_2 + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4 + 2\,NH_4Cl.$$

For titration—

$$5\,CaC_2O_4 + 8\,H_2SO_4 + 2\,KMnO_4 \rightarrow 5\,CaSO_4 + 2\,MnSO_4 + K_2SO_4 + 10\,CO_2 + 8\,H_2O.$$

*Reagents.*

1. *Dilute hydrochloric acid (1:1)* prepared by adding 1 volume of concentrated hydrochloric acid to 1 volume of water.
2. *Methyl red indicator* (see p. 72).
3. *Ammonium oxalate solution* prepared by dissolving 4 grams of $(NH_4)_2C_2O_4 \cdot H_2O$ in water and diluting to a 100 ml. volume.

4. *Dilute ammonium hydroxide solution (1:1)* prepared by adding 1 volume of concentrated ammonium hydroxide to 1 volume of water.
5. *Dilute sulfuric acid (1:1)* prepared by slowly adding 1 volume of concentrated sulfuric acid to 1 volume of $H_2O$.
6. *Standard 0.1 N potassium permanganate solution.*

*Procedure.* Weigh accurately a portion of about one gram of the sample into a 250 ml. beaker and dissolve it in the smallest possible volume of dilute hydrochloric acid. Heat, if necessary, to effect complete solution. Carefully transfer to a 250 ml. volumetric flask with the aid of a wash bottle. Cool to room temperature, dilute to the exact volume and mix thoroughly.

With the aid of a calibrated 50 ml. bulb pipette, remove two 50.00 ml. aliquots into 400 ml. beakers, add 150 ml. of water and 2 drops of methyl red indicator. Heat the solution to boiling and while hot add slowly, with vigorous stirring, the required amount of ammonium oxalate solution. The amount of ammonium oxalate solution used should be in excess of the amount sufficient to precipitate all the calcium present. Calculate the volume of ammonium oxalate solution required to precipitate all the calcium as calcium oxalate, assuming the sample to be pure calcium carbonate. To insure an excess, add 5 ml. of solution to the amount calculated. After adding the precipitating agent, add dilute ammonium hydroxide drop by drop with constant stirring until the indicator turns light yellow (just slightly alkaline). Cover the beakers with watch glasses and digest for one hour or longer on the steam bath.

Decant the supernatant liquid through a prepared Gooch crucible using suction. Wash the precipitate several times with hot water and finally transfer the precipitate into the crucible. Continue washing the crucible and contents until a sample of the filtrate, when heated and acidified with sulfuric acid, does not cause decolorization of an added drop of potassium permanganate solution (the precipitate is then free from soluble oxalate ion).

Place the crucible and contents in a beaker, add 150 ml. of water and 15 ml. of dilute sulfuric acid (1:1). By means of a stirring rod, thoroughly disintegrate the asbestos mat in the crucible to insure that all the precipitate goes into solution. Heat the solution almost to boiling and while hot titrate with the standard potassium permanganate solution until the first permanent noticeable pink color is obtained. Stir the solution vigorously throughout the addition of the permanganate solution.

Calculate the percentage of calcium present in the sample from the volume of standard potassium permanganate used in the titration and the weight of sample present in the aliquot analyzed.

**Standardization Against a Primary Standard—Iron Wire.** In standardizing a solution it is a good rule, whenever possible, to use as a primary standard a substance which is similar to the material which will be determined by the standardized solution. Thus, for the determination of iron, it is preferable to standardize the permanganate solution against pure iron.

Pure iron wire is dissolved in sulfuric acid forming a solution of ferrous sulfate and ferric sulfate, since some oxidation occurs during solution. The ferric iron is reduced to the ferrous state and the total reduced iron solution titrated by the permanganate solution to be standardized. The reduction of the ferric iron is accomplished by running the solution through a Jones reductor.

*Jones Reductor.* A Jones reductor (Fig. 16) is prepared in the following manner: Secure a reductor tube (approximately 2 cm. in diameter and 50 cm. long) with an enlarged top and a stopcock at the bottom. Place a loose plug of glass wool in the bottom of the tube and then a layer of acid-washed asbestos slightly thicker than that used in a Gooch crucible. Water should flow through the mat readily (75–100 ml. per min.) without applying suction.

Prepare sufficient amalgamated zinc for the reductor in the following manner: Dissolve 5 grams of mercury in a dilute nitric acid solution (25 ml. of concentrated nitric acid plus 25 ml. of water). Dilute with 250 ml. of water and add 400–500 grams of 20–30 mesh analyzed grade zinc. Stir for 5–10 min., pour off the solution and thoroughly wash the zinc by decantation until the washings no longer give an acid reaction. Keep the zinc under water at all times.

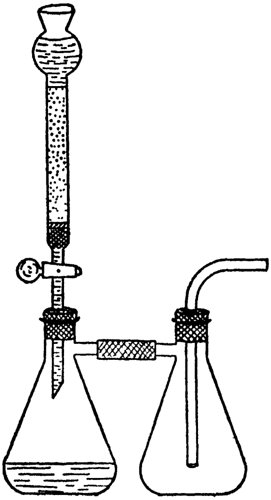

FIG. 16. Diagram of a Jones Reductor.

Place a column of about 35–40 cm. of the amalgamated zinc in the reductor tube on top of the asbestos plug. Immediately plug the top loosely with glass wool and fill the tube with distilled water. Mark the tube 3 cm. above the zinc layer as a point below which liquid must never be allowed to fall as air should never come in contact with the zinc column.

Support the column as illustrated in Fig. 16, in a suction flask by means of a rubber stopper. Connect the suction flask to a second suction flask or safety bottle as a precaution to prevent water from backing up into the first suction flask if a water pump is used.

A blank determination is made to ascertain if the reductor is operating properly. Start the suction, partly open the stopcock at the bottom of the reductor tube and draw 100 ml. of water through the column at 25–50 ml. per minute, taking care that the water level never falls below the mark above the zinc layer. Discard the water in the suction flask.

In a similar manner, pass 200 ml. of 2 N sulfuric acid, followed by 100 ml. of water through the reductor. Be sure that air does not come in contact with the zinc at this step as hydrogen peroxide will be formed which would later react with permanganate. Remove the suction flask and test the contents by dropping in 1–2 drops of standard permanganate solution from a burette. If the pink color from the permanganate is evident, the reductor is ready for use. If the color is dissipated, further acid and water washings are made until a pink permanganate color persists when 1–2 drops are added to the washings.

*Preparation of an Approximately 0.1 N Ferrous Salt Solution.* Crystallized ferrous sulfate, $FeSO_4 \cdot 7\ H_2O$, or ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O$, may be used to prepare the ferrous salt solution. The reaction involved in the titration of ferrous sulfate with potassium permanganate is:

$$2\ KMnO_4 + 10\ FeSO_4 + 8\ H_2SO_4 \rightarrow 5\ Fe_2(SO_4)_3 + 2\ MnSO_4 + K_2SO_4 + 8\ H_2O.$$

Since ten moles of ferrous sulfate react with two moles or ten equivalent weights of potassium permanganate, one equivalent weight of potassium permanganate will react with one mole of ferrous sulfate (its equivalent weight). In terms of electron transfers and valence change, it is noted that each ferrous atom loses an electron (valence change of one) when it is oxidized to the ferric state. The equivalent weight of ferrous sulfate would thus be its molecular weight, i.e., for $FeSO_4 \cdot 7\ H_2O$, 278.0; and for $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O$, 392.2.

Weigh 28 grams of the hydrated ferrous sulfate or 40 grams of the ferrous ammonium sulfate into a liter volumetric flask. Dissolve in water and dilute to the mark.

Determine the volume ratio of the permanganate solution to the ferrous sulfate solution as follows: Place each of the solutions in a burette. Remove exactly a 30 ml. sample of the ferrous sulfate solution, add 15 ml. of 2 N sulfuric acid, dilute to 100 ml. and titrate with permanganate until the solution has a faint pink color due to a slight excess of permanganate. Repeat until replicate determinations agree. In reading the burette containing the permanganate it is more convenient to read from the top of the meniscus than from the bottom. Calculate the volume ratio of the permanganate solution to the ferrous sulfate solution.

*Standardization Procedure.* Weigh accurately three 0.2–0.25 gram pieces of pure iron wire free from rust and carefully wiped with filter paper. Dissolve each sample of iron wire in 100 ml. of 2 N sulfuric acid and boil for a few minutes.

Pass this iron solution, at the rate of 25–50 ml. per minute, through the reductor which has been previously washed and does not have a blank titration of over 2 drops of standard permanganate solution. Wash the beaker and the reductor with 100 ml. of 2 N sulfuric acid followed by washing with 100 ml. of water, taking care throughout that the liquid layer never falls below the mark above the zinc layer.

Remove the suction flask, cool, and titrate immediately with the permanganate solution until a permanent pink color is apparent. If the end point is overstepped, add a measured volume of the ferrous sulfate solution to give a slight excess, and titrate the excess with the permanganate solution. This excess of ferrous sulfate may be corrected for readily, since the volume ratio of the permanganate solution to the ferrous sulfate solution has been previously determined.

Obtain the titration values for the three iron wire samples prepared, correcting the values if ferrous sulfate was used in the titration, and also for the blank value of the reductor. Calculate the normal factor of the potassium permanganate solution.

**Determination of Iron in an Iron Ore.** Grind small portions of the sample in a mortar. Weigh accurately, samples of 0.4–0.5 gram each into procelain crucibles and heat at a dull red heat for 30 min. to destroy any organic matter present. Cool the crucibles, place each in an evaporating dish, add 25 ml. of approximately 20 per cent hydrochloric acid and heat until the samples are dissolved. Remove the crucibles, rinsing with a small amount of water.

The hydrochloric acid must be removed before the solution is passed through the reductor. Add 5 ml. of concentrated sulfuric acid and heat on the steam bath. When the solution is clear, continue the heating on a hot plate until white $SO_3$ fumes are given off. Cool, add 100 ml. of water and heat the solution. Pass this solution through the Jones reductor in exactly the same manner as the iron wire solutions in the standardization of the permanganate. Titrate with the standard permanganate solution and calculate the percentage of iron in the ore for each of the samples.

## DICHROMATE METHODS

Potassium dichromate functions as an oxidizing agent because of the oxidizing ability of the chromium in the $Cr_2O_7^{=}$ ion: $\overset{+++}{\mathrm{Cr}^{+++}} \xrightarrow{+3\epsilon} \mathrm{Cr}^{+++}$. In the oxidation, each chromium atom gains three electrons (valence change of 3). The equivalent weight of potassium dichromate ($K_2Cr_2O_7$), containing two chromium atoms would then be its molecular weight (294.2) divided by six or 49.03.

Relatively few volumetric oxidation-reduction methods involve the use of dichromate as an oxidizing agent. The determination of iron when in the reduced form and, conversely, the determination of chromium by standard iron solutions are the most important of the methods.

**Preparation of One Liter of 0.1 N Potassium Dichromate Solution.** Potassium dichromate may be obtained in a sufficiently pure form to be used as a primary standard and requiring only a preliminary drying before use. However, for very accurate work, it is adivisable to standardize the solution against a pure substance of the same nature as the substance being determined.

Dry a sample of pure potassium dichromate for 2 hours or longer at 160°–180° C., and cool in a desiccator. Weigh accurately, 4.903 grams of the dry sample and transfer to a calibrated liter volumetric flask. Dissolve in water and dilute to the mark. If a high grade sample of potassium dichromate was used, the solution should be exactly 0.1 N and need not be standardized.

**Preparation of One Liter of Approximately 0.1 N Ferrous Salt Solution.** Crystallized ferrous sulfate, $FeSO_4 \cdot 7\,H_2O$, or ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$, may be used to prepare the ferrous salt solution. The reaction involved in the titration of ferrous sulfate with potassium dichromate is:

$$6\,FeSO_4 + K_2Cr_2O_7 + 7\,H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + K_2SO_4 + 7\,H_2O.$$

Since each ferrous atom loses one electron (valence change of one) when it is oxidized to the ferric state, the equivalent weight of ferrous sulfate is its molecular weight, i.e., for $FeSO_4 \cdot 7\ H_2O$, 278.0; and for $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O$, 392.2.

Weigh 28 grams of the hydrated ferrous sulfate or 40 grams of the ferrous ammonium sulfate into a liter volumetric flask. Dissolve in water, add 5–10 ml. of concentrated hydrochloric acid and dilute to the mark. The resulting solution is approximately 0.1 N.

*Indicators.* The end point in a titration of a ferrous solution by a standard dichromate solution may be determined by either an outside (external) or an internal indicator. The outside indicator used almost exclusively is a dilute potassium ferricyanide solution. This indicator should be prepared freshly before use by dissolving a crystal of potassium ferricyanide 1–2 mm. in diameter in 25 ml. of water. A drop of this indicator solution placed on a spot plate will turn blue if brought into contact with any ferrous ion and brownish if all the iron is in the oxidized state.

Titrations involving an outside indicator are more time consuming than when an internal indicator is used. Consequently, there has been a renewed interest in dichromate oxidations with the discovery of good internal oxidation indicators. Of these, either the sodium or barium salt of diphenylamine sulfonic acid[1, 2] is usually selected. To prepare an indicator solution of 0.01 molar diphenylamine sodium sulfonate, dissolve 3.2 grams of the barium salt in water, dilute to a liter, add a slight excess of sodium sulfate, and decant or filter the solution. The indicator changes from colorless to a violet purple when all the iron has been oxidized.

**Determination of the Volume Ratio of the Potassium Dichromate Solution to the Ferrous Sulfate Solution.** Either the ferricyanide or diphenylamine indicator may be used in this titration. If diphenylamine is used, add 3–4 drops of the indicator to the titration solution. However, in order to illustrate the use of an outside indicator, the method discussed will involve the use of ferricyanide indicator.

Thoroughly clean two burettes, rinse, and fill one with the ferrous salt solution and the other with the potassium dichromate solution. Accurately measure 40 ml. of the ferrous solution into a 400 ml. beaker, add 100 ml. of water and 20 ml. of dilute hydrochloric acid solution (10 ml. of concentrated acid: 10 ml. of water). Run into this solution 35 ml. of the dichromate solution (5 ml. less

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[1] Sarver and Kolthoff, *J. Am. Chem. Soc.*, **53**, 2902 (1931).

[2] Willard and Young, *Ind. Eng. Chem., Anal. Ed.*, **5**, 154 (1933).

than the calculated required volume), stirring vigorously throughout the addition.

Test for the end point of the titration in the following manner: Place a drop of the ferricyanide indicator solution into each depression of a spot plate. Dip the end of a glass rod in the reaction solution and transfer a small drop of the solution into the indicator on the spot plate. If a blue color results, indicating the presence of ferrous ions, add 0.5 ml. of the dichromate solution to the reaction flask and test again. Continue the titration in this manner until the blue color on the spot plate becomes faint. Then add the dichromate solution dropwise, testing for the end point after the addition of each drop. Confirm the end point by determining that the blue color does not appear within one minute after the addition of a drop of solution to the indicator on the spot plate.

If, at any time, the end point is overrun, add more ferrous sulfate solution and continue the titration with the dichromate solution. Calculate the volume ratio of the potassium dichromate solution to the ferrous sulfate solution. Repeat until replicate determinations check.

**Standardization of the Potassium Dichromate Solution against a Primary Standard—Iron Wire.** Electrolytic iron or iron wire of high purity is dissolved in hot dilute hydrochloric acid forming ferrous chloride. However in the process, some of the iron is oxidized by the air to the ferric state making it necessary to reduce it to the ferrous state. This is accomplished by the addition of stannous chloride, the excess of which is removed by mercuric chloride since stannous chloride would react with dichromate. The mercurous chloride formed is not oxidized by potassium dichromate while the ferrous iron is oxidized. The reactions involved are:

$$2\,FeCl_3 + SnCl_2 + 2\,HCl \rightarrow 2\,FeCl_2 + H_2SnCl_6$$

$$SnCl_2 + 2\,HgCl_2 + 2\,HCl \rightarrow Hg_2Cl_2 + H_2SnCl_6$$

$$6\,FeCl_2 + K_2Cr_2O_7 + 14\,HCl \rightarrow 6\,FeCl_3 + 2\,KCl + 2\,CrCl_3 + 7\,H_2O.$$

*Reagents.*

1. *Approximately 20 per cent hydrochloric acid solution* prepared by adding 40 ml. of concentrated hydrochloric acid to 55 ml. of water.
2. *Stannous chloride solution* prepared by dissolving 50 grams of stannous chloride in 100 ml. of concentrated hydrochloric acid and diluting to a volume of one liter with water.
3. *Mercuric chloride solution* prepared by making a saturated solution of mercuric chloride in water.

*Procedure.* Weigh accurately three 0.2–0.25 gram pieces of the pure iron wire free from rust and carefully wiped with filter paper. Heat 30 ml. of the approximately 20 per cent hydrochloric acid solution to boiling in a 500 ml. Erlenmeyer flask. Remove from the flame, drop a weighed sample of the iron wire into the acid and immediately cover the flask with a short-stem glass funnel. Boil until the wire is dissolved, then wash down the funnel and the sides of the flask with a small amount of hot water. Add, drop by drop, by means of a pipette, a solution of stannous chloride to the hot iron solution until it turns just colorless, and then add just one drop in excess (a larger excess will liberate mercury, which, in turn will reduce ferric chloride formed in a later reaction and so cause erroneous results). Add 200 ml. of water and cool. Add 10 ml. of saturated mercuric chloride solution to the cold iron solution, let stand for three minutes, and titrate with the potassium dichromate solution.

*Titration Using Ferricyanide Indicator* (*Outside Indicator*). From a burette, run about 35 ml. of the potassium dichromate solution into the reduced iron solution and conduct the titration in a manner similar to that used for determining the volume ratio of potassium dichromate to ferrous sulfate. If the end point is passed, add a measured volume of the ferrous sulfate solution, titrate to the end point, and correct for the volume of ferrous sulfate added, making use of the volume ratio data previously secured. Calculate the normal factor of the potassium dichromate solution.

*Titration Using Diphenylamine Sulfonic Acid Indicator* (*Internal Indicator*). Add 5 ml. of 85 per cent phosphoric acid solution (to repress the concentration of ferric ion by forming a complex ion since, in a high concentration of ferric ion, the end point is not sharp due to the oxidation of indicator by ferric ions) to the solution and 5–7 drops of diphenylamine sulfonic acid indicator. Titrate with the dichromate solution, adding it slowly with constant stirring, until the color begins to change. Then add the dichromate solution, drop by drop, until a violet purple tinge is noted. The reaction goes slowly and care must be taken so that the end point is not passed. Conduct a blank determination and correct for this value in the final calculation. Calculate the normal factor of the potassium dichromate solution.

**Determination of Percentage Iron in an Iron Ore.** Iron ores contain primarily the iron oxides $Fe_2O_3$ and $Fe_3O_4$, some silica, small amounts of other elements, and sometimes organic matter. Since certain of the possible metallic contaminants interfere with reduction methods other than the stannous chloride method, or else affect an oxidizing agent such as potassium permanganate, the stannous chloride reduction method followed by titration with standard dichromate is the process commonly used for the analysis of iron ores. If organic matter is present it must be destroyed by incineration at a dull red heat.

Grind small portions of the sample in a mortar. Weigh accurately a sample of about 0.3 gram into a porcelain crucible and heat at a dull red heat for 30 min. to destroy any organic matter present. Cool the crucible and pour the contents into a 500 ml. Erlenmeyer flask. Dissolve any of the sample remaining in the crucible with a little hydrochloric acid, adding it to the contents of the flask, and then rinse the crucible with a little water. Add sufficient 20 per cent hydrochloric acid to the flask so that the total acid added, including that used for washing the crucible, will be 10–15 ml. Add 3 ml. of saturated stannous chloride solution (the addition of stannous chloride at this step aids in the solution of the ore). Digest on a steam bath, adding small amounts of the approximately 20 per cent hydrochloric acid solution as the volume in the flask decreases. When the sample has completely disintegrated, evident by a white residue, dilute to 20 ml., heat almost to boiling and slowly drop in the stannous chloride solution until all the iron is reduced, as shown by the absence of the yellow color of the ferric ion. Add 1 drop of stannous chloride solution in excess, cool thoroughly and add 10 ml. of saturated mercuric chloride solution. Let stand 5 min. and dilute with 200 ml. of 3 N sulfuric acid. Add 5 ml. of 85 per cent phosphoric acid solution, 5–7 drops of diphenylamine sulfonic acid indicator solution, and titrate as in the standardization of the dichromate solution using an internal indicator. Calculate the percentage of iron in the sample of ore.

## CERIC SULFATE METHODS

A more recently developed oxidizing agent is ceric sulfate. This reagent has approximately the same oxidation potential as potassium permanganate and may be substituted for it in all titrations. There is, however, the necessity of using a catalyst in some reactions while permanganate requires none. Ceric sulfate is always used in acid solution since ceric hydroxide will precipitate out in alkaline solutions.

The advantages possessed by ceric sulfate as an oxidizing agent are: Solutions of this substance are stable in concentrations of 0.01 N or greater. The ceric ion, in acid solution, undergoes but one reaction—namely, a change in valence from +4 to +3 ($Ce^{++++} \rightarrow Ce^{+++}$). The reduced cerous ion is colorless and so does not interfere with indicator colors. The bottom of the meniscus may be read in ceric solutions up to a concentration of 0.1 N. It is possible to employ ceric sulfate in relatively high hydrochloric acid concentrations without danger of oxidation of the chloride ion.

**Indicator.** The most commonly used indicator in ceric oxidations is ferrous orthophenanthroline.[1] The indicator is prepared by adding a solution of orthophenanthroline to a ferrous salt. The color changes from a deep red to a faint blue.

To prepare the indicator solution, weigh out 14.85 grams of orthophenanthroline monohydrate and dissolve it in one liter of 0.025 molar freshly prepared ferrous sulfate solution. Use 1 drop of the indicator solution in a titration volume of 100–150 ml.

**Preparation of an Approximately 0.1 N Ceric Sulfate Solution.** When used as an oxidizing agent in acid solution, the ceric ion goes from a valence of +4 to a valence of +3. Its equivalent weight is therefore its molecular weight. Weigh out 40.4 grams of ceric sulfate, $Ce(SO_4)_2 \cdot 4\,H_2O$, or 63.3 grams of the dihydrate of ceric ammonium sulfate, $Ce(SO_4)_2 \cdot 2\,(NH_4)_2SO_4 \cdot 2\,H_2O$, dissolve in 500 ml. of 2 N sulfuric acid and dilute to one liter of solution. If the solution is not clear filter through asbestos. Preserve in a glass stoppered bottle.

**Standardization against a Primary Standard—Iron Wire.** Ceric sulfate solutions may be standardized against the primary standards arsenious oxide, sodium oxalate, and iron wire. Since ceric sulfate is most frequently used in iron determinations, the standardization with iron wire will be the only method discussed here.

*Reagents.*

1. *Stannous chloride solution* prepared by dissolving 50 grams of stannous chloride in 100 ml. of concentrated hydrochloric acid and diluting to a volume of one liter with water.
2. *Saturated mercuric chloride solution* prepared by making a saturated solution of mercuric chloride in water.

*Procedure.* Weigh accurately three 0.2–0.25 gram pieces of pure iron wire, free from rust, and carefully wiped with filter paper. Transfer to 500 ml. Erlenmeyer flasks and dissolve in 10 ml. of hydrochloric acid, covering each flask with a small watch glass to prevent any loss through spattering. When the wire has dissolved, rinse off the watch glass, heat nearly to boiling and add, drop by drop, a stannous chloride solution until the solution is decolorized. Do not add more than one drop in excess of the stannous chloride solution. Cool thoroughly, and add rapidly 10 ml. of a saturated mercuric chloride solution. Let stand 4–5 min., add 10 ml. of hydrochloric acid, and dilute to a volume of approximately 300 ml. Add 2 drops of the ferrous orthophenanthroline indicator solution and titrate to a color change from orange red to faint yellow or greenish yellow. It is advisable to determine an indicator blank and correct the titration for this value. Calculate the normal factor of the ceric sulfate solution as determined by each sample of iron wire and average.

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[1] Walden, Hammett, and Chapman, *J. Am. Chem. Soc.*, 55, 2649 (1933).

**Determination of Percentage Iron in an Iron Ore.** Prepare and dissolve the sample as in the determination with potassium dichromate (p. 97). After complete reduction with stannous chloride, add rapidly 10 ml. of saturated mercuric chloride solution. Let stand 4–5 min., add 10 ml. of hydrochloric acid and dilute to a volume of approximately 300 ml. Add 2 drops of the ferrous orthophenanthroline indicator and titrate to the end point with the standard ceric sulfate solution. Calculate the percentage of iron in the ore sample.

## IODOMETRIC METHODS

Iodometric methods are volumetric methods involving iodine or its compounds. Iodine itself is a good oxidizing agent, while the iodide ion is a good reducing agent and will react with a number of oxidized substances to liberate free iodine. Those methods which use an iodine solution as an oxidizing agent may be termed direct iodometric methods. Those methods involving the action of an oxidized substance on potassium iodide to liberate free iodine, which is subsequently determined, are known as indirect iodometric methods.

**Direct Iodometric Methods.** Iodine is a direct oxidizing agent in neutral or slightly acid solutions. Best results are obtained in the *p*H range from 4–9. Iodine cannot be used in the presence of caustic alkalies or the normal carbonates since it reacts with these substances.

A few common reactions in which iodine is used as a direct oxidizing agent are:

$$Na_2SO_3 + I_2 + H_2O \rightarrow Na_2SO_4 + 2\,HI$$

$$2\,Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2\,NaI$$

$$Na_3AsO_3 + I_2 + 2\,NaHCO_3 \rightarrow Na_3AsO_4 + 2\,NaI + 2\,CO_2 + H_2O.$$

**Indirect Iodometric Methods.** Iodine may be used indirectly in the analysis of substances which are stronger oxidizing agents than iodine. In these reactions the iodide ion is added in considerable excess so as to insure complete reduction of the oxidizing agent.

A few common reactions which form the basis for indirect iodometric methods are:

$$2\,KMnO_4 + 10\,KI + 8\,H_2SO_4 \rightarrow 6\,K_2SO_4 + 2\,MnSO_4 + 5\,I_2 + 8\,H_2O$$

$$K_2Cr_2O_7 + 6\,KI + 14\,HCl \rightarrow 2\,CrCl_3 + 8\,KCl + 3\,I_2 + 7\,H_2O$$

$$KIO_3 + 6\,KI + 6\,HCl \rightarrow KI + 6\,KCl + 3\,I_2 + 3\,H_2O$$

$$H_2O_2 + 2\,KI + H_2SO_4 \rightarrow K_2SO_4 + I_2 + 2\,H_2O$$

$$2\,CuSO_4 + 4\,KI \rightarrow Cu_2I_2 + I_2 + 2\,H_2O.$$

**Starch Indicator for Iodometric Titrations.** Molecular iodine itself is colored and might conceivably be used as its own indicator for the end point of a titration. However, this is usually not done and the iodine color is simply used as an indication that the end point is approaching. Then a starch suspension is added which gives an intense blue color with iodine and a colorless solution when all the iodine has been removed, providing a much more sensitive end point than the iodine color alone.

The starch indicator solution should be freshly prepared or else preserved by the addition of mercuric iodide. Starch solutions which have stood for several days hydrolyze and, in the presence of iodine, give a reddish-violet color which does not disappear entirely at the end point of the titration. The blue starch-iodine color is likely due to the adsorption of iodine on the colloidal starch particles. Heat decreases this adsorption so that titrations using starch as an indicator should be made in the cold. Furthermore, the starch indicator should not be added in the titration until the concentration of iodine is relatively low. If considerable iodine is present, sufficient adsorption takes place to remove appreciable iodine from solution. Then, as the end point of the titration nears, the adsorbed iodine goes back into solution slowly and the end point is not sharp.

Prepare the starch indicator solution as follows: Make a starch suspension by stirring 1 gram of soluble starch into 10 ml. of water. Pour this well mixed suspension into 100 ml. of boiling distilled water, stir thoroughly, and continue the heating for 2 min. Cool, and if a precipitate settles out, decant the supernatant liquid and use as the indicator solution.

**Preparation of an Approximately 0.1 N Iodine Solution.** In the reaction:

$$Na_2SO_3 + I_2 + H_2O \rightarrow Na_2SO_4 + 2\ HI$$
$$I_2{}^0 \rightarrow 2\ I^-$$

neutral iodine is reduced to iodide ion, resulting in a valence change of one for each atom of iodine. Therefore, a normal solution of iodine must contain one atomic weight of iodine (126.9 grams) per liter of solution. A 0.1 N solution will contain one tenth of this quantity or 12.69 grams of iodine per liter of solution.

Weigh approximately 12.7 grams of resublimed iodine into a 400 ml. beaker. Add about 20 grams of potassium iodide and dissolve with thorough stirring in as little water as possible. Transfer to a liter volumetric flask and dilute to volume. Store in a glass-stoppered dark bottle and insure that the solution does not come into contact with organic matter or dust.

Iodine is but slightly soluble in water but is quite soluble in a solution of potassium iodide. The iodine and iodide ion from potassium iodide apparently combine to form a complex ion ($I_2 + I^- \rightarrow I_3{}^-$). This complex ion in an aqueous solution also has a lower vapor pressure than an aqueous iodine solution and so tends to keep the iodine from volatilizing. Iodine dissolved in a potassium iodide solution behaves as though it were only an iodine solution and is considered as such for all practical purposes.

**Standardization of Iodine Solution Against a Primary Standard—Arsenious Oxide ($As_2O_3$).** Arsenious oxide is an excellent primary standard for the direct standardization of iodine solutions. It may be obtained readily in a pure form and is not appreciably affected by the atmosphere. It is usually advisable, however, to dry the oxide to insure that it is entirely moisture free. Arsenious oxide, in a highly purified form, for use as a primary standard may be obtained from the United States Bureau of Standards. The following equation is useful in calculating the equivalent weight of arsenious oxide:

$$As_2{}^{+++}O_3{}^{=} + O_2 \rightarrow As_2{}^{\overset{++}{+++}}\ O_5{}^{=}.$$

The valence change for each arsenic atom is from +3 to +5. Since two arsenic atoms are concerned in each molecule, the total valence change is 4. The equivalent weight of arsenious oxide is then:

$$\frac{As_2O_3}{4} = \frac{197.9}{4} = 49.475.$$

Weigh accurately 0.12–0.15 of a gram of pure, dry arsenious oxide into a 300 ml. Erlenmeyer flask. Add 100 ml. of a 2 per cent sodium hydroxide solution and warm gently on the steam bath to bring the arsenious oxide into solution. To this solution add a few drops of phenolphthalein indicator and neutralize with dilute hydrochloric acid, adding an excess of 2–3 drops of the acid. Next add about 5 grams of sodium bicarbonate *in small amounts at first,* so as not to cause the solution to foam up over the side of the flask. Titrate with the iodine solution until the end point is nearly reached (this may be calculated from the amount of arsenious oxide sample, assuming the iodine solution to be 0.1 N, or it can be estimated by the rate at which the drops of added iodine solution are decolorized, or else determined by a preliminary rough titration). Add 5 ml. of starch indicator solution and continue the titration with the iodine until a slight blue color persists for a minute. From the volume of iodine solution added and the weight of the arsenious oxide sample, calculate the normal factor of the iodine solution.

*Remarks.* Arsenious oxide dissolves readily in caustic alkali to give an arsenite:

$$As_2O_3 + 6\,NaOH \rightarrow 2\,Na_3AsO_3 + 3\,H_2O.$$

Iodine, however, reacts with caustic alkalies to form a hypoiodite:

$$2\,NaOH + I_2 \rightarrow NaIO + NaI + H_2O.$$

For this reason any sodium hydroxide in excess of that required to form sodium arsenite must be neutralized with hydrochloric acid.

Sodium bicarbonate is added to neutralize the excess acid added. It also prevents the formation of any HI in the oxidation of sodium arsenite by iodine and so permits the reaction to go to completion. Such a bicarbonate buffered solution, when saturated with carbonic acid, has a $pH$ of approximately 7.

$$Na_3AsO_3 + I_2 + H_2O \rightleftarrows Na_3AsO_4 + 2\,HI$$

but when $NaHCO_3$ is added:

$$Na_3AsO_3 + I_2 + NaHCO_3 \rightarrow Na_3AsO_4 + 2\,NaI + 2\,CO_2 + H_2O.$$

**Standardization of the Iodine Solution by Titration Against a Standard Sodium Thiosulfate Solution.** If a sodium thiosulfate solution of known normality is available, it offers a rapid means of determining the normality of an iodine solution. The iodine solution may be titrated directly by the standard thiosulfate solution using starch indicator as the end point approaches. From the volume ratio of the two solutions and the known normal factor of the thiosulfate solution, the normal factor of the iodine solution may readily be calculated.

**Preparation of an Approximately 0.1 N Sodium Thiosulfate Solution.** From the reaction: $2\ Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2\ NaI$, it is obvious that one iodine atom oxidizes (and hence is equivalent to) one sodium thiosulfate molecule. Since the equivalent weight of iodine is its atomic weight, then the equivalent weight of sodium thiosulfate must be one molecular weight of the thiosulfate or 158 grams. A liter of 0.1 N solution will then require 15.8 grams of anhydrous sodium thiosulfate or 24.8 grams of crystalline sodium thiosulfate ($Na_2S_2O_3 \cdot 5\ H_2O$). Weigh out the required amount of sodium thiosulfate, transfer to a liter volumetric flask, dissolve in water, and dilute to the mark.

**Standardization of the Sodium Thiosulfate Solution by Titration Against a Standard Iodine Solution.** Sodium thiosulfate solutions may be standardized by direct titration against an iodine solution, previously standardized against arsenious oxide. In the procedure, a known volume of iodine solution is titrated with the thiosulfate solution until the iodine color becomes faint. Then starch indicator solution is added and the titration continued until the solution becomes colorless. From the volume ratio of the two solutions and the known normal factor of the iodine solution, calculate the normal factor of the thiosulfate solution.

**Standardization of the Sodium Thiosulfate Solution Against a Primary Standard—Copper.** An indirect iodometric method for the standardization of sodium thiosulfate solutions uses metallic copper as a primary standard. This method depends upon the liberation of an atom of iodine by each atom of copper present when a solution of a cupric salt is treated with an excess of potassium iodide.

$$2\ Cu^{++} + 4\ I^- \rightarrow Cu_2{}^+I_2{}^- + I_2.$$

Since each atom of copper liberates one atom of iodine, and the equivalent weight of iodine is its atomic weight, then the equivalent weight of copper is its atomic weight or 63.57 grams. This same conclusion can be reached by another line of reasoning. The copper atom with a valence of +2 is reduced to a valence of +1, therefore the equivalent weight of copper is its atomic weight.

*Reagents.*

1. *Nitric acid solution (1:1).* To a definite volume of water add an equal volume of concentrated nitric acid.

2. *Potassium iodide solution.* Dissolve 40 grams of potassium iodide in water, dilute to 100 ml. and make the solution slightly alkaline to avoid the formation of hydriodic acid and its oxidation products.
3. *Starch indicator solution* (see p. 101).
4. *Sodium acetate solution.* Dissolve 574 grams of the trihydrate and dilute to a liter of solution.

*Procedure.* Weigh accurately 0.2–0.4 gram of pure carefully cleaned copper and transfer to a 300 ml. Erlenmeyer flask graduated roughly at 20 ml. intervals. Dissolve the copper in 5 ml. of a 1:1 nitric acid solution, dilute to 20–30 ml., boil to expel the red fumes, add a slight excess of strong bromine water and boil until the bromine is completely driven off. Cool, and add 10 ml. of the sodium acetate solution which buffers the effect of the nitric acid and liberates some acetic acid. Add sufficient potassium iodide solution, slowly and with constant agitation, so that at the end of the titration the concentration of potassium iodide will be 4.0–4.5 grams per 100 ml.

Titrate with the thiosulfate solution until the brown color becomes faint. Add freshly prepared starch indicator solution and continue the titration until the blue starch-iodine color just disappears. Add approximately 2 grams of ammonium thiocyanate, thoroughly dissolve it in the solution, then continue the titration to the disappearance of the blue color. From the weight of copper taken and the volume of thiosulfate solution used, calculate the normal factor of the thiosulfate solution and also its equivalence in milligrams of copper.

**Standardization of the Sodium Thiosulfate Solution Using Potassium Dichromate as a Primary Standard.** Potassium dichromate is obtained in sufficiently pure form to be used as a primary standard when thoroughly dried. An indirect iodometric method makes its use possible as a primary standard in determining the normality of a thiosulfate solution. The reactions involved in this method are:

$$K_2Cr_2O_7 + 6\,KI + 14\,HCl \rightarrow 2\,CrCl_3 + 8\,KCl + 3\,I_2 + 7\,H_2O$$

$$I_2 + 2\,Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2\,NaI.$$

In general, the method involves making a solution of potassium iodide, then the addition of carbonate and acid to produce carbon dioxide which replaces the air in the container and thereby decreases the amount of air in contact with the solution. Enough acid must be added to neutralize all the carbonate and create a sufficiently high acid concentration to permit a rapid oxidation of the iodide ion by the dichromate. Addition of a measured volume of dichromate solution causes the liberation of a corresponding stoichiometrical quantity of iodine. The container is covered with a watch glass to prevent loss of iodine and is placed in the desk to eliminate any decomposition by light. Dilution of the solution before titration with thiosulfate is necessary to reduce the H-ion concentration. The liberated iodine is titrated by the thiosulfate solution using starch indicator and the normal factor calculated.

*Procedure.* Place 2–3 grams of the pure potassium dichromate in a flat-type weighing bottle and dry for 2 hours or longer at 160°–180° C. Cover the dish and cool in a desiccator. Weigh out accurately 1.2–1.4 grams of the dry sample, transfer to a calibrated 250 ml. volumetric flask, dissolve in water and dilute to the mark.

Place 100 ml. of water in a 500 ml. Erlenmeyer flask, add 5 grams of potassium iodide and shake until dissolved. Dissolve in this solution, with shaking, 2.0 grams of sodium carbonate and then add 7–8 ml. of concentrated hydrochloric acid.

Remove, by means of a calibrated bulb pipette, a 25 ml. aliquot of the potassium dichromate solution and slowly run it into the solution in the Erlenmeyer flask, mixing the solutions thoroughly by gentle rotation of the flask throughout the addition of the dichromate. Cover with a small watch glass and place the flask in the desk for 5–10 min. to allow completion of the reaction liberating iodine. Remove the flask from the desk, rinse off the watch glass, and dilute the solution to a volume of approximately 300 ml. with water.

Titrate the liberated iodine with the thiosulfate solution until the iodine color becomes faint. Add 3–5 ml. of starch indicator solution and titrate until the blue starch-iodine color just disappears and the solution acquires a green color due to the chromic ion. Calculate the normal factor of the thiosulfate solution.

**Determination of Arsenious Oxide ($As_2O_3$) in Arsenic Samples.** Samples of arsenic containing up to 40 per cent arsenious oxide may be purchased or prepared for class use. These samples should contain no substances which will interfere with the solution and direct titration of the arsenious oxide by a standard iodine solution.

*Reagents.*

1. *A 2 per cent sodium hydroxide solution* prepared by dissolving 2 grams of sodium hydroxide in 98 grams of water.

2. *An approximately 20 per cent sulfuric acid solution* prepared by adding 12 ml. of the concentrated acid to 78 ml. of water
3. *Starch indicator solution* (see p. 101).
4. *Standard 0.1 N iodine solution.*

*Procedure.* Accurately weigh several samples of approximately 0.4 gram into 300 ml. Erlenmeyer flasks. Add to each sample 50 ml. of a 2 per cent sodium hydroxide solution and heat to effect solution of the sample.

Cool the solution and add 10 ml. of a 20 per cent sulfuric acid solution. Again cool the solution and carefully add sodium bicarbonate, in small portions, until the acid is neutralized, then add an excess of the bicarbonate. Dilute the solution to 150 ml. and titrate with a standard 0.1 N iodine solution until the end point is almost reached, i.e., when the iodine color disappears much more slowly than at the beginning of the titration. Add 2 ml. of a 1 per cent starch indicator solution and titrate until the end point is reached when the blue starch-iodine color persists for at least 10 sec. Calculate and report the arsenic present in the sample as percentage of arsenious oxide ($As_2O_3$).

# CHAPTER VIII

## VOLUMETRIC PRECIPITATION METHODS

Volumetric precipitation methods differ from the volumetric methods previously discussed in that an insoluble precipitate is formed upon titration. In order that the method be strictly quantitative, this precipitation reaction must go to practical completion. The end point of the reaction is indicated, as in other volumetric methods, by a suitable indicator. Since but few suitable indicators are available for these methods, the number of volumetric precipitation methods is relatively small.

**The Determination of Chloride.** Two volumetric precipitation methods, the Mohr and the Volhard methods, are available for the determination of chlorides. The Mohr method is used when chloride is to be determined in a relatively pure solution. When other substances are present in addition to the chloride, the Volhard method must be employed.

### THE MOHR METHOD

In the Mohr method, the chloride is titrated directly by a standard silver nitrate solution using potassium chromate as an indicator. The method is restricted to halide salts of comparatively strong bases including ammonium and magnesium salts. Substances, other than the halide to be determined, which form slightly soluble silver salts, must be absent These would include cyanides, sulfocyanides, other halides, sulfides, phosphates and arsenates. Barium, iron and lead form insoluble chromates so they must also be absent. The halide solution to be titrated must be neutral. If acid, silver chromate will not precipitate at the end point; if alkaline, silver oxides will precipitate. If the solution is alkaline, it is made acid with nitric acid and neutralized with calcium carbonate. Under these conditions, an excess of calcium carbonate is added to serve as a buffer in the titration.

**Preparation of an Approximately 0.1 N Silver Nitrate Solution.** The equivalent (normal) weight of silver nitrate is obtained by dividing its molecular weight (169.89) by the valence (1) of the precipitating ion (silver). A 0.1 N solution would then contain 16.989 grams. Weigh out 17 grams of silver nitrate on a rough balance, dissolve, and dilute to a volume of one liter with distilled water.

**Standardization of the Approximately 0.1 N Silver Nitrate Solution Against a Primary Standard, Potassium Chloride, Using the Mohr Method.** The reactions occurring in this titration which form the basis for this method are:

$$(1)\ AgNO_3 + KCl \rightarrow AgCl + KNO_3.$$

$$(2)\ 2\,AgNO_3 + K_2CrO_4 \rightarrow Ag_2CrO_4 + 2\,KNO_3.$$

$$(3)\ Ag_2CrO_4 + 2\,KCl \rightarrow K_2CrO_4 + 2\,AgCl.$$

When the silver nitrate solution is added to the neutral chloride solution, silver chloride is formed and precipitates from the solution. As soon as all the chloride has reacted with the silver nitrate, the next drop of silver nitrate in the presence of potassium chromate indicator, precipitates silver chromate which imparts a reddish-orange color to the solution. In fact, as the titration progresses and before the end point is reached, the red silver chromate precipitate is observed as the silver nitrate solution is run into the chloride solution. However, since the silver chromate is more soluble than the silver chloride, it reacts with the soluble chloride according to reaction (3). Since the silver chromate is not very soluble, the reaction is slow, and so considerable stirring and time are required near the end point of the titration.

*Procedure.* Heat some pure potassium chloride for one hour or longer at 140° C., cool in a desiccator, and accurately weigh three samples between 0.15–0.2 gram each into 250 ml. beakers. Dissolve the potassium chloride in 50 ml. of water and add, as indicator, 2–3 drops of a saturated potassium chromate solution. Place the beaker and contents on a white surface and titrate with the silver nitrate solution, with constant stirring, until the first permanent pink-orange color change is observed. Great care should be exercised and sufficient time taken as the end point is approached so that the correct result may be obtained. Calculate the normal factor of the solution.

## THE VOLHARD METHOD

Since the Mohr method is restricted to relatively pure solutions of halides the Volhard method is used most extensively for the titration of chlorides in samples of material. Volhard's original method involved the treatment of the sample with an excess of standard silver nitrate solution and the immediate titration of the excess silver nitrate with a standard potassium thiocyanate solution using ferric alum indicator. With large quantities of chloride present the results are satisfactory, but with small amounts of chlorides the results are too high. This is due to the fact that the end point in the titration is not permanent because the silver chloride formed is more soluble than the silver thiocyanate and so the following reaction takes place:

$$AgCl + KCNS \rightarrow AgCNS + KCl.$$

To eliminate this difficulty, the precipitated silver chloride is filtered off or treated in such a way that it cannot react with potassium thiocyanate before the titration of the excess silver nitrate. Heating alone will coagulate the precipitate and thereby reduce the surface exposed to the solution. The addition of organic liquids such as ethyl ether, acetone, toluene, xylene, benzene, and nitrobenzene just previous to the titration with thiocyanate aid in coagulating and surrounding the silver chloride precipitate so that it cannot react.

*Reagents.*

1. *Nitric acid solution* (4:1), prepared by adding 4 volumes of concentrated nitric acid to 1 volume of water.
2. *Ferric alum indicator.* A saturated solution of ferric ammonium alum.
3. *Standard 0.1 N silver nitrate solution.* Previously prepared and standardized by the Mohr method.

*Preparation of an Approximately 0.1 N Potassium Thiocyanate Solution.* From the reaction: $AgNO_3 + KSCN \rightarrow AgSCN + KNO_3$, it is noted that one equivalent weight of silver nitrate reacts with one equivalent weight of potassium thiocyanate, therefore a normal solution would contain a molecular weight of potassium thiocyanate in a liter of solution. A 0.1 N solution would contain one-tenth as much or 9.718 grams per liter. Weigh out 10 grams of potassium thiocyanate, dissolve in water and dilute to a liter of solution.

*Standardization of an Approximately 0.1 N Potassium Thiocyanate Solution Against a Standard Silver Nitrate Solution.* From a burette, run out 25.00 ml. of the standard silver nitrate solution into a beaker. Dilute with 100 ml. of water, add 5 ml. of the 4:1 nitric acid solution and 5 ml. of the ferric alum indicator. The reaction must be acid to prevent the hydrolysis of the ferric salts. Place the beaker on a white surface and titrate with the potassium thiocyanate solution until the first detectable permanent pink coloration is obtained, stirring constantly throughout the titration. Calculate the normal factor of the solution.

The reactions involved in the titration are:

(1) $AgNO_3 + KCNS \rightarrow AgCNS + KNO_3$.

(2) $6\,KCNS + Fe_2(SO_4)_3 \rightarrow 2\,Fe(CNS)_3 + 3\,K_2SO_4$.

**Determination of Chloride in a Sample of Soluble Chloride.** Weigh accurately into 400 ml. beakers duplicate samples of 0.15–0.2 gram of the soluble chloride (the sample must not exceed 0.2 gram). Dissolve in 50 ml. of water and add exactly 50 ml. of the standard 0.1 N silver nitrate solution. Carefully acidify the solution with dilute nitric acid, heat to boiling and filter, collecting the filtrate in a clean 400 ml. beaker. Wash the precipitate free from nitrates, collecting all the wash water in the same beaker containing the filtrate from that particular sample. The filtrate and washings should have a volume of 150–200 ml. Add 5 ml. of the 4:1 nitric acid solution, 5 ml. of the ferric alum indicator solution, and titrate the excess silver nitrate with standard thiocyanate solution. From the titration value obtained calculate the percentage of chloride present in the sample.

**Determination of the Sodium Chloride Content of Meat or Cheese.** The weighed sample is disintegrated in water and sufficient measured standard silver nitrate solution is added to react with all the chloride present and also leave an excess of silver nitrate. The organic matter is oxidized by heating with nitric acid and potassium permanganate. After cooling, the precipitated silver chloride is prevented from any further reaction by the addition of acetone. The excess silver nitrate is then determined by titration with standard potassium thiocyanate solution using ferric alum indicator and the chloride content calculated.

*Procedure.* Weigh three 5.0 gram samples of the product (weigh to the nearest tenth of a gram) and place each sample in a 300 ml. Erlenmeyer flask. (For class work, the instructor may add a measured volume of salt solution of definite concentration to two of the samples, leaving the third sample as a control or blank. It is then possible for the student to determine and report the amount of added sodium chloride to the two samples.)

Add to each flask 25 ml. of distilled water, shake, and add exactly 50.0 ml. of the standard 0.1 N silver nitrate solution. This amount of silver nitrate must be sufficient to react with all the chloride present and leave an excess of the silver nitrate. If the quantity proves insufficient, a new sample must be weighed out and sufficient silver nitrate added before the sample is digested. Shake thoroughly, and add 10 ml. of saturated potassium permanganate solution, followed by 25 ml. of concentrated nitric acid.

Boil the mixture under a hood until all the organic matter is oxidized. It may be necessary in some cases to add 10 ml. more of saturated potassium permanganate to complete the oxidation.

Cool the mixture and add sufficient distilled water to bring the volume in the flask to approximately 150 ml. Add 10 ml. of acetone, 1 ml. of ferric alum indicator, and titrate the excess silver nitrate with the standard 0.1 N potassium thiocyanate solution. The acetone prevents the precipitated silver chloride from reacting with the potassium thiocyanate, thus eliminating the necessity of filtering off the silver chloride in order to obtain a definite end point. Calculate the chloride present in the sample as percentage of sodium chloride.

# PART IV

# ANALYSIS BY PHYSICAL CHEMICAL METHODS

## CHAPTER IX

## PHYSICAL CHEMICAL METHODS

Physical chemical methods are being used more and more extensively in quantitative analysis. This is due to the high degree of accuracy attainable and the speed with which many of these determinations may be made. In addition, certain information is gained by these methods which could not be obtained by any other method of analysis.

### SPECIFIC GRAVITY

The agricultural chemist is usually concerned with the determination of the specific gravity of liquids rather than solids. For this reason, the following discussion will be limited to the specific gravity of liquids.

Specific gravity is ordinarily defined as the ratio of the weight of a definite volume of a substance at a definite temperature to the weight of the same volume of water at 4° C. This value expresses the true specific gravity at that temperature for the substance in question and is synonymous with density, since the density of water at approximately 4° C. is unity. Thus we may use the true specific gravity value of a liquid as the weight of 1 ml. of that liquid. True specific gravity is expressed as:

$$\text{Sp. Gr.}\tfrac{t^\circ}{4^\circ}$$

where $t^\circ$ is the temperature of the liquid.

Due to the experimental difficulty in working at 4° C., a more convenient temperature is usually employed when making the actual specific gravity determination. We commonly obtain the ratio of the weight of a definite volume of a substance at $t^\circ$ to the weight of the same volume of water at the same temperature. The value is then expressed as, Sp. Gr.$\tfrac{t^\circ}{t^\circ}$, and is known as relative or apparent specific gravity. In many types of work, the relative specific gravity gives all the necessary information. In the event that the true specific gravity is desired, it may be obtained by multiplying the relative specific gravity by the density of water at $t°$ (Table 8).

TABLE 8. RELATIVE DENSITY OF WATER AT DIFFERENT TEMPERATURES

| Temperature, °C. | Density | Temperature, °C. | Density |
|---|---|---|---|
| 0 | .99987 | 17 | .99881 |
| 4 | 1.00000 | 18 | .99863 |
| 5 | .99999 | 19 | .99844 |
| 6 | .99997 | 20 | .99823 |
| 7 | .99993 | 21 | .99802 |
| 8 | .99988 | 22 | .99780 |
| 9 | .99981 | 23 | .99757 |
| 10 | .99973 | 24 | .99733 |
| 11 | .99964 | 25 | .99707 |
| 12 | .99953 | 26 | .99681 |
| 13 | .99941 | 27 | .99654 |
| 14 | .99928 | 28 | .99626 |
| 15 | .99913 | 29 | .99597 |
| 16 | .99898 | 30 | .99567 |

The ordinary methods for the determination of specific gravity are based upon either a ratio of weights of equal volumes, or a ratio of volumes of equal weights. The pycnometer and Westphal balance methods are based upon a ratio of weights of equal volumes, while the hydrometer method is based upon a ratio of volumes of equal weights.

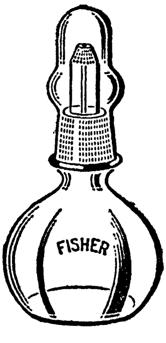

FIG. 17. Pycnometer or Specific Gravity Bottle. (Courtesy of Fisher Scientific Co.)

**Pycnometer Method.** This method is based upon a comparison of weights of equal volumes of liquid and water at $t°$ C. The pycnometer (Fig. 17) is a vessel designed to contain always a definite volume of liquid at a definite temperature. Its use permits the most accurate determination of the specific gravity of a liquid.

*Types of Pycnometers.* Various types of pycnometers are available. Of these, the pycnometer bottle diagramed in Fig. 17 is one of the simplest. Such a bottle may be modified by having the ground glass stopper on the top equipped with a thermometer to read the temperature of the liquid in the bottle. A side arm capillary tube is then built on the bottle by which the volume of liquid contained is adjusted. The Sprengel-Ostwald tube is diagramed in Fig. 18. Liquid may be drawn into the tube and the correct temperature attained by hanging the tube in a water bath. The excess liquid in the tube may then be blown out, the tube hung on the balance, and weighed.

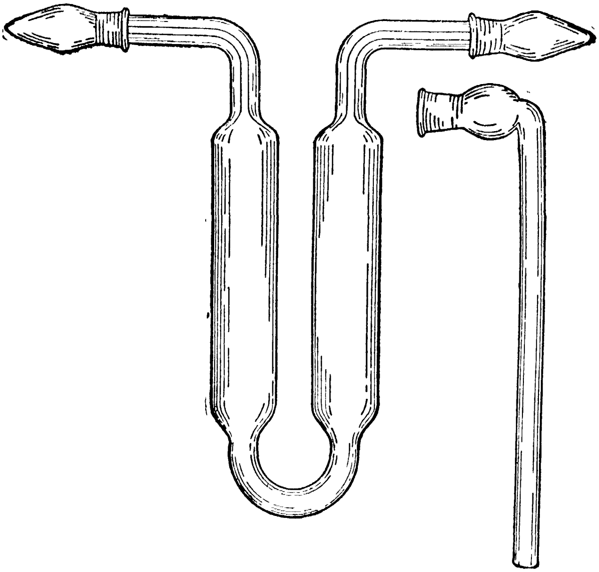

FIG. 18. Sprengel-Ostwald Tube. (From Thurston's "Pharmaceutical and Food Analysis," D. Van Nostrand Co., Inc.)

*Procedure.* Obtain the weight of a thoroughly cleaned and dried pycnometer. Completely fill the pycnometer with recently boiled distilled water (free from air), at a temperature 2–3 degrees lower than that at which the specific gravity is to be determined. Force the stopper into the pycnometer and place the bottle in a water bath held at the desired temperature. Water should be forced out through the capillary in the stopper at this temperature thus insuring the complete filling of the capillary tube in the stopper. After the pycnometer and contents have attained the temperature of the bath (20–30 min.), the drop of water on the top of the stopper is quickly wiped off with a piece of filter paper (do not keep the filter paper in contact with the top of the stopper or it will draw some of the water out of the capillary). Remove the pycnometer from the bath and dry thoroughly with a cloth. Place the cap over the stopper as soon as possible after removing the pycnometer from the bath to reduce the amount of evaporation.

Weigh the pycnometer containing the water as soon as the outside of the bottle has been wiped dry. In a similar manner, fill the pycnometer with the liquid to be tested, adjust to the correct temperature in a water bath, dry and weigh. Then:

$$\text{Sp. Gr.}\frac{t^\circ}{t^\circ} = \frac{\text{Wt. pcynometer and liquid at } t^\circ - \text{Wt. dry pycnometer}}{\text{Wt. pycnometer and water at } t^\circ - \text{Wt. dry pycnometer}}.$$

Multiplying the value obtained by the density of water at $t^\circ$, gives the true specific gravity of the liquid.

For very accurate work it is necessary to correct this specific gravity value for the buoyancy of the air by taking into account the density of the latter. Considering this correction, the expression for the specific gravity of a liquid would be:

$$\text{Sp. Gr.}\frac{t^\circ}{4^\circ} = \frac{W^1 D}{W} - \frac{0.0012\,(W^1 - W)}{W}.$$

In the event that the temperature of the water and the other liquid when weighed in the pycnometer is not the same, a further correction for the expansion of glass is required. The general expression for the specific gravity of a liquid including the corrections for buoyancy of air and expansion of glass would be:

$$\text{Sp. Gr.}\frac{t^\circ}{4^\circ} = \frac{W^1 D}{W} - \frac{0.0012\,(W^1 - W)}{W} + \frac{W^1 D}{W} \times 0.000024\,(t - t^1)$$

where: $W$ = the apparent weight of water in air at temperature $t$; $W^1$ = the apparent weight of the liquid in air at temperature $t^1$; $D$ = the relative density of water at temperature $t$; 0.000024 = the coefficient of cubical expansion of glass; 0.0012 = the mean density of air.

**Westphal Balance Method.** Archimedes' principle, "A solid submerged in a liquid will lose in weight equal to the weight of the volume of liquid displaced," is the basis for this method. A plummet of constant volume is submerged in water at $t^\circ$ and the loss in weight of the plummet is determined. This loss in weight represents the weight of water displaced at $t^\circ$. In a similar manner the loss in weight of the plummet when submerged in a liquid at $t^\circ$ will give the weight of the liquid displaced at $t^\circ$. The ratio of the weight of liquid displaced at $t^\circ$ to the weight of water displaced at $t^\circ$ will give the relative specific gravity (Sp. Gr.$\frac{t^\circ}{t^\circ}$) of the liquid. The Westphal balance is constructed to read relative specific gravity at 15.5° C., so all determinations should be made at this temperature. For only a few liquids, correction tables are available so that determinations may be made at other temperatures and corrected to 15.5° C.

*Construction of the Westphal Balance.* The Westphal balance (Fig. 19) consists of a beam balanced on a knife-edge which in turn is supported on a stand equipped with a leveling screw. A glass plummet is suspended from one end of the beam and counterpoised on the other end of the beam by a fixed brass weight. The plummet is of such a size that at 15.5° C. it will displace exactly 5.0 grams of water. The beam is graduated between the knife-edge and the point of the plummet suspension into ten equal divisions. Placing a 5 gram rider on the tenth division (the point from which the plummet is suspended) the balance should be in equilibrium in water at 15.5° C. and the specific gravity would be 1. Placing a 5 gram rider on any of the other divisions would indicate the tenths of specific gravity, e.g., if placed on the eighth division it would represent a specific gravity of 0.8. In a similar manner the 0.5 gram rider determines the hundredths, the .05 gram rider determines the thousandths and the .005 gram rider determines the ten-thousandths of the specific gravity reading.

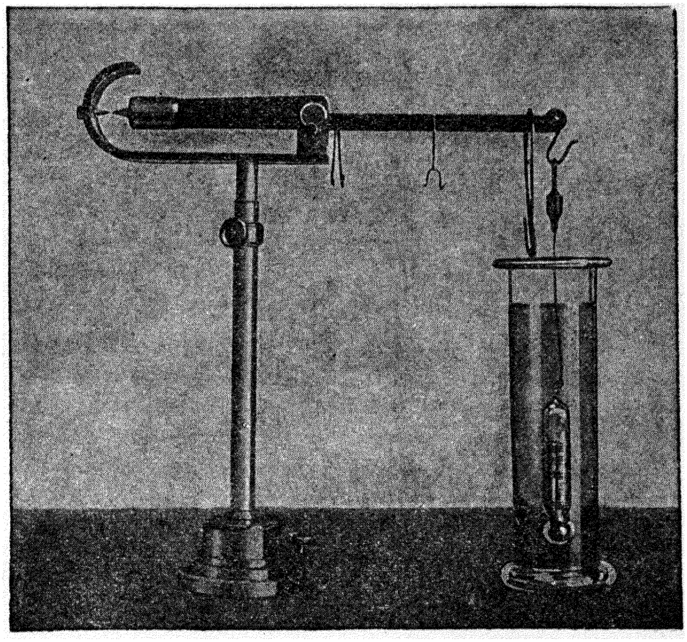

FIG. 19. Westphal Balance. (From Jacobs' "Chemical Analysis of Foods and Food Products," D. Van Nostrand Co., Inc.)

*Procedure.* By means of the leveling screw at the base of stand, adjust the balance with the plummet suspended in air, so that the beam is horizontal as indicated by the pointer at one end of the beam. The liquid, cooled to 15.5° C., is poured into a glass cylinder. To maintain a temperature of 15.5° C. it is advisable to hold the cylinder in a water bath at 15.5° C. The cylinder and contents are then placed under the beam so that the suspended plummet is *entirely submerged* in the liquid and no air bubbles adhere to the plummet. A 5 gram rider is placed on the tenth scale division (the hook from which the plummet is suspended) for liquids heavier than water. The other 5 gram rider is placed on that beam division where it will be too light to effect an exact balance but would be too heavy if placed on the next higher division. The two 5 gram riders give the unit and first decimal readings for the specific gravity. The same procedure is followed successively with the 0.5 gram, then the 0.05 gram and finally the 0.005 gram riders to give the second, third and fourth decimal readings, respectively, for the relative specific gravity of the sample. If two riders should occupy the same position on the beam, suspend the smaller rider from the larger one.

Westphal balances are calibrated to read relative specific gravities at 15.5° C. only, i. e., Sp. Gr.$\frac{15.5°}{15.5°}$. This value may be corrected to true specific gravity by multiplying by the density of water at 15.5° C. The instrument cannot be used to read specific gravities at other temperatures unless calibrated for that temperature or a table of corrections for the liquid in question is available.

**Hydrometer Method.** The method is based upon the comparison of volumes of equal weights of liquid and water. Archimedes' principle also applies to this method: "A solid suspended in a liquid will be buoyed up by a force equal to the weight of the liquid displaced."

*Construction of the Hydrometer.* The hydrometer or weighted spindle (Fig. 20) has a constant weight. When suspended in a liquid, it will sink to a depth where the weight of the liquid displaced equals the weight of the hydrometer. In a liquid of low density, the hydrometer will, of necessity, sink to a greater depth than in a heavier more dense liquid, so that an equal weight of liquid is displaced in each case.

The stem of the hydrometer is calibrated to read specific gravity directly when used at a specified temperature (usually 15.5° C.). The value obtained is the apparent or relative specific gravity of the liquid, i. e., Sp. Gr.$\frac{15.5°}{15.5°}$.

Hydrometers are graduated to read wide and narrow ranges of specific gravity. For example, a hydrometer is available to read specific gravities of liquids lighter than water and another to read specific gravities of liquids heavier than water. Obviously, those graduated for such a wide range of specific gravities cannot be read as accurately as those covering a narrow range. Hydrometers covering a wide range of specific gravity are frequently used to determine the approximate specific gravity of a liquid. The accurate specific gravity may then be determined by selecting a hydrometer whose graduations cover the range of the approximate specific gravity previously determined.

Special hydrometers are constructed to give readings other than specific gravity values. Baumé hydrometers read in degrees Baumé. For liquids heavier than water, Baumé degrees may be converted into specific gravity values by the following formula: Sp. Gr. $= \frac{145}{145 - \text{Be}^\circ}$. For liquids lighter than water, the conversion formula is: Sp. Gr. $= \frac{140}{130 + \text{Be}^\circ}$. The Quevenne lactometer, used in milk, reads from 15 to 40° corresponding to specific gravities of 1.015 to 1.040. The New York Board of Health lactometer is graduated into arbitrary degrees, where 0° corresponds to a specific gravity of 1.000, and 100° to a specific gravity of 1.029. These two types of hydrometers cover the restricted range of specific gravities normally encountered in milk. Brix hydrometers are used in sugar work and read directly the percentage of sucrose in solutions. Other special hydrometers are Twaddell, alcoholometer, urinometer, etc.

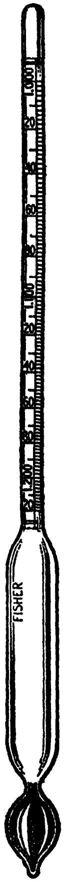

FIG. 20. Hydrometer. (Courtesy of Fisher Scientific Co.)

*Procedure.* The liquid is cooled to 15.5° C. and placed in a cylinder somewhat larger in diameter than the diameter of the hydrometer bulb. The hydrometer is gently lowered into the liquid, pushed slightly below the equilibrium point to overcome the effects of viscosity and surface tension, and then allowed to come to rest. The reading is taken on the stem of the hydrometer at the level of the liquid in the cylinder (not the height to which liquid "creeps" on the stem of the hydrometer). The temperature of the liquid must be maintained at 15.5° C. in order to read the relative specific gravity directly from the hydrometer. In the case of a few special types of hydrometers, correction tables may be found which will permit the use of those hydrometers at temperatures other than the one for which they are calibrated.

The true specific gravity value may be obtained by multiplying the relative specific gravity read at 15.5° C. by the density of water at 15.5° C.

## REFRACTOMETRY

A beam of light passing obliquely from one medium into another of different optical density is refracted, the degree of refraction being such that the ratio of the sines of the angles of incidence and refraction is constant and characteristic for the two media at a given temperature and pressure, Fig. 21. According to the wave theory of light, the ratio of the velocities of light in the two media is identical with the ratio of the sines of the angles of incidence and refraction. This ratio is referred to as the index of refraction, denoted by the letter $n$. If the angles of incidence and refraction are represented by $i$ and $r$, respectively, and the velocities of light in the two media are represented by $v$ and $v_1$, the expression for refractive index may be written:

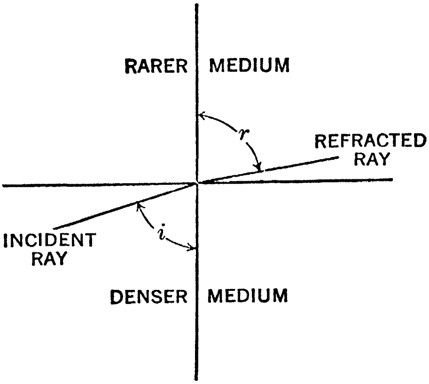

FIG. 21. Diagram of Refraction of Light when Passing from One Medium into Another.

$$n = \frac{v}{v_1} = \frac{\sin i}{\sin r}.$$

It is customary to refer the refractive index of a liquid to air. However, in the actual determination, a refractometer with a glass prism is used and the index of refraction for glass to liquid is determined. The index of refraction for the liquid to air is then obtained by multiplying the refractive index of glass to liquid by the refractive index of glass to air.

The refractive index value varies with the wave length of light since light of short wave lengths is refracted more than that of longer wave lengths. Thus it is necessary to employ monochromatic light of definite wave length and indicate the character of the light in expressing the index of refraction. Sodium light (*D* line of the spectrum) is commonly used. If white light is used, a series of prisms must be introduced into the system to correct for the dispersion obtained.

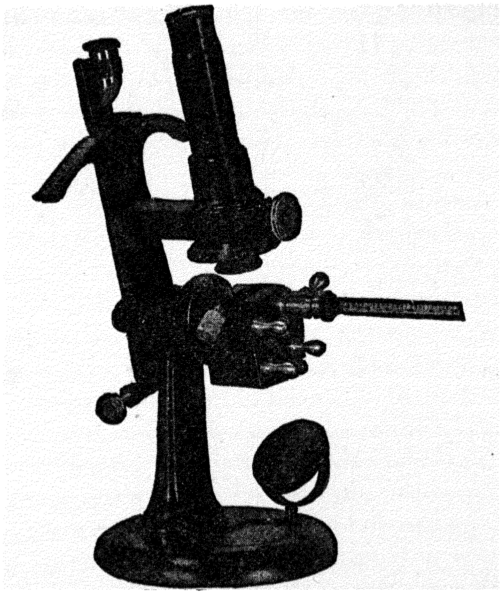

Fig. 22. Abbe Refractometer. (Courtesy of Bausch and Lomb.)

Instruments designed to measure the refractive index of liquids are known as refractometers. Of the various types of refractometers on the market, the Abbe and the immersion types are perhaps the most widely known and generally used.

**Abbe Refractometer.** The Abbe type of refractometer, Fig. 22, possesses several advantages over other types of refractometers. It permits the determination of a wide range of refractive indices—1.3 to 1.7. Only a few drops of liquid are required for a sample and either white or monochromatic light can be used. The refractive index can be read quickly and easily with an accuracy of about ±.0002.

The Abbe refractometer consists essentially of two glass prisms having a refractive index of 1.75, a telescope provided with cross hairs and including also a compensator made up of two Amici prisms. The Amici prisms make it possible to use white light since the prisms serve to merge the rays, dispersed by the liquid according to their wave lengths, into one path—that of the sodium wave length (*D* line of the spectrum). A sector divided into proportionate parts, representing refractive indices from 1.3 to 1.7 *referred to air*, completes the assembly.

*Procedure.* Open the prism box and place a few drops of the liquid upon the ground surface of the lower prism. Close and securely fasten the prism box again, insuring that a sufficient quantity of the liquid remains between the prisms (it may be necessary to tilt the refractometer somewhat before closing the box to prevent the liquid from flowing off the prism before the box is closed). Focus the cross hairs of the telescope by rotating the eyepiece and adjust the mirror so as to obtain good illumination. By means of the arm at the side of the apparatus, turn the prism box slowly backwards and forwards until the lower part of the field of view is dark and the upper part light. A sharp line of demarcation between the fields is obtained by turning the milled screw-head on the telescope which rotates the "compensator" (consisting of two prisms, which revolve in opposite directions, and so form a system of variable dispersion) until the colored fringe disappears and a clear, definite boundary appears. Move the prism box until this clearly defined boundary line coincides with the intersection of the cross hairs in the telescope, and read off directly the index of refraction referred to air on the divided sector. A direct reading to the third decimal place is obtained and the fourth decimal place may be estimated with an accuracy of ±0.0002.

The prisms are enclosed in a jacket through which water can be circulated to regulate the temperature which is read on a thermometer screwed into the end of the prism box. Accurate temperature control is best obtained by circulating water through the jacket by means of a pump from a water bath, the temperature of which is accurately controlled by a thermostat.

**The Immersion or Dipping Refractometer.** The basic principles concerned in the immersion type of refractometer are the same as those for the Abbe type.

The immersion type of refractometer, Fig. 23, consists of three essential units: an immersion prism, a compensator, and a telescope equipped with a scale. This instrument is more accurate than the Abbe type since it covers a much more restricted field of refractive indices. The earlier instruments read refractive indices only from 1.32 to 1.36. By using interchangeable prisms, however, the range may be extended up to a refractive index of 1.54. A larger sample of liquid is required than in the Abbe since sufficient liquid must be present to cover the prism after immersion. Scale readings on this instrument may be converted to indices of refraction with the aid of Table 9.

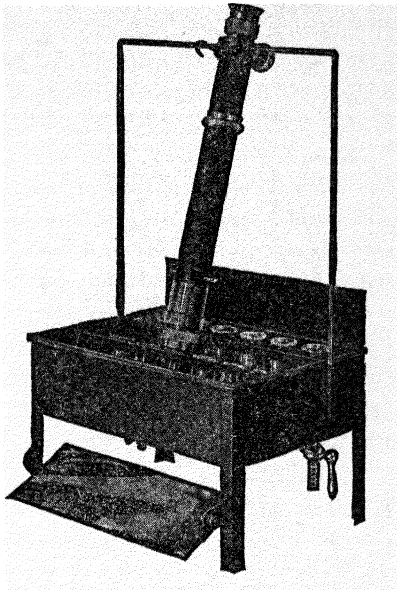

Fig. 23. Immersion Refractometer. (Courtesy of Bausch and Lomb.)

*Procedure.* A small beaker full of the liquid to be tested is placed in the holder of a special type of water bath having a frosted-glass plate cemented into its bottom, and equipped with a mirror to reflect light through the frosted-glass plate and through the beaker containing the liquid. A metal support to hold the refractometer in the proper position is also attached to the water bath. About a 10-min. immersion of the sample in the bath is required for it to attain the temperature of the bath.

The refractometer is hung from the support with the prism immersed in the sample contained in the beaker. The mirror on the

TABLE 9. INDICES OF REFRACTION CORRESPONDING TO READINGS ON THE IMMERSION REFRACTOMETER

| Scale reading | |
|---|---|
| 0 | 1.32736 |
| 1 | 1.32775 |
| 2 | 1.32814 |
| 3 | 1.32854 |
| 4 | 1.32893 |
| 5 | 1.32932 |
| 6 | 1.32971 |
| 7 | 1.33010 |
| 8 | 1.33049 |
| 9 | 1.33087 |
| 10 | 1.33126 |
| 11 | 1.33165 |
| 12 | 1.33204 |
| 13 | 1.33242 |
| 14 | 1.33281 |
| 15 | 1.33320 |
| 16 | 1.33358 |
| 17 | 1.33397 |
| 18 | 1.33435 |
| 19 | 1.33474 |
| 20 | 1.33513 |
| 21 | 1.33551 |
| 22 | 1.33590 |
| 23 | 1.33628 |
| 24 | 1.33667 |
| 25 | 1.33705 |
| 26 | 1.33743 |
| 27 | 1.33781 |
| 28 | 1.33820 |
| 29 | 1.33858 |
| 30 | 1.33896 |
| 31 | 1.33934 |
| 32 | 1.33972 |
| 33 | 1.34010 |
| 34 | 1.34048 |
| 35 | 1.34086 |
| 36 | 1.34124 |
| 37 | 1.34162 |
| 38 | 1.34199 |
| 39 | 1.34237 |
| 40 | 1.34275 |
| 41 | 1.34313 |
| 42 | 1.34350 |
| 43 | 1.34388 |
| 44 | 1.34426 |
| 45 | 1.34463 |
| 46 | 1.34500 |
| 47 | 1.34537 |
| 48 | 1.34575 |
| 49 | 1.34612 |
| 50 | 1.34650 |
| 51 | 1.34687 |
| 52 | 1.34724 |
| 53 | 1.34761 |
| 54 | 1.34798 |
| 55 | 1.34836 |
| 56 | 1.34873 |
| 57 | 1.34910 |
| 58 | 1.34947 |
| 59 | 1.34984 |
| 60 | 1.35021 |
| 61 | 1.35058 |
| 62 | 1.35095 |
| 63 | 1.35132 |
| 64 | 1.35169 |
| 65 | 1.35205 |
| 66 | 1.35242 |
| 67 | 1.35279 |
| 68 | 1.35316 |
| 69 | 1.35352 |
| 70 | 1.35388 |
| 71 | 1.35425 |
| 72 | 1.35461 |
| 73 | 1.35497 |
| 74 | 1.35533 |
| 75 | 1.35569 |
| 76 | 1.35606 |
| 77 | 1.35642 |
| 78 | 1.35678 |
| 79 | 1.35714 |
| 80 | 1.35750 |
| 81 | 1.35786 |
| 82 | 1.35822 |
| 83 | 1.35858 |
| 84 | 1.35894 |
| 85 | 1.35930 |
| 86 | 1.35966 |
| 87 | 1.36002 |
| 88 | 1.36038 |
| 89 | 1.36074 |
| 90 | 1.36109 |
| 91 | 1.36145 |
| 92 | 1.36181 |
| 93 | 1.36217 |
| 94 | 1.36252 |
| 95 | 1.36287 |
| 96 | 1.36323 |
| 97 | 1.36359 |
| 98 | 1.36394 |
| 99 | 1.36429 |
| 100 | 1.36464 |

bath is adjusted so that the proper amount of light is reflected through the sample, into the prism of the refractometer, and illuminates the upper portion of the field of view of the telescope. The compensating Amici prisms are then adjusted to give a clear-cut separation between the lower dark field (totally reflected light) and the upper light field viewed in the telescope. The eyepiece of the telescope may also require focusing so that the scale reading may be accurately determined. With the micrometer screw set at 0, the reading is determined on the scale viewed in the telescope where the line of demarcation between the light and dark fields crosses the graduated scale. If the line comes between two of the scale division, the unit reading taken is the last whole division above the point at which the boundary line crosses the scale. By adjusting the micrometer screw until the boundary line exactly coincides with a scale division, the first decimal place may be read directly and the second place estimated from the graduations on the micrometer drum.

The refractometer, when correctly adjusted, should give the following readings on distilled water: 15.5 at 15° C., 15.0 at 17.5° C., 14.5 at 20° C., and 13.25 at 25° C. If, upon checking the instrument against distilled water at one of the foregoing temperatures, the reading differs by more than 0.1 scale division from the correct reading, the instrument should be adjusted[1] or the proper correction applied to every reading made.

## COLORIMETRY

Colorimetric determinations have been found extremely valuable for the quantitative determination of small amounts of a constituent. For larger amounts, when gravimetric or volumetric methods are available, they are most commonly used since colorimetric methods are usually less applicable and also less accurate. Colorimetric methods are adapted to the determination of small quantities of material, consequently the dilution required to bring larger quantities within the range of colorimetric methods will greatly magnify any error in the determination.

Colorimetric methods are more rapid than the gravimetric and volumetric methods available for the same determination. Thus, if speed is the determining factor, colorimetric methods may be selected in preference to the others. The choice of the method, then, is governed largely by the relative amount of constituent to be determined and the speed with which the determination may be made.

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[1] Browne and Zerban, "Sugar Analysis," John Wiley & Sons, Inc., 3d Ed., (1941), p. 119.

A disadvantage of colorimetric methods employing a visual colorimeter is that many persons are unable to compare colors accurately. This is especially true for certain colors, notably yellow. In addition, tint as well as color is measured in the colorimeter so that a color-blind person has considerable difficulty in comparing colors. These difficulties due to individuals are, of course, eliminated by the use of the photoelectric colorimeter.

Beer's law, which is the basis of all colorimetric work, states that the intensity of light transmitted by a color solution is a function of the concentration of the solute and the depth of solution under observation; the transmission being less as the concentration and depth of solution increases. Then:

$$\log T_1 = kd_1c_1$$
$$\log T_2 = kd_2c_2$$

where

$T_1$ = transmitted light intensity of known solution;
$T_2$ = transmitted light intensity of unknown solution;
$d_1$ = depth of known solution (read on colorimeter);
$d_2$ = depth of unknown solution (read on colorimeter);
$c_1$ = concentration of known solution;
$c_2$ = concentration of unknown solution;
$k$ = proportionality constant.

When the light transmitted through both sides of the colorimeter is the same intensity:

$$T_1 = T_2 \text{ and } d_1c_1 = d_2c_2 \text{ or } c_2 = \frac{d_1c_1}{d_2}.$$

Beer's law assumes that the degree of dissociation of the colored solute does not change with concentration, and also that there is no dissociation, rearrangement, or combination of the colored solute with the solvent to give products of a different hue. Since this assumption is not always true, Beer's law may not hold when the concentrations of the known and unknown solutions compared in the colorimeter are far apart. This difficulty may be overcome by changing the concentration of the known solution until it approaches that of the unknown solution, or by the application of a previously determined correction factor.

**The Visual Colorimeter.** The essential parts of a visual colorimeter are a source of light, two cups into which the solutions to be compared are placed, two prisms, and a lens system to conduct the transmitted light to the eyepiece in which is observed a split field for matching the light intensity transmitted through the two solutions (Fig. 24). The cups are attached to a mechanism which permits them to be raised or lowered, thereby varying the depth of solution through which the light passes, and two scales for measuring the depths of the two solutions.

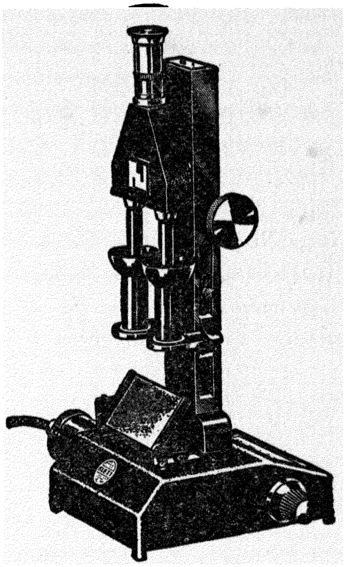

FIG. 24. Visual Colorimeter. (Courtesy of Fisher Scientific Co.)

The known solution is placed in one cup and the unknown solution in the other. The cups are raised so that the prisms are immersed in the solutions, taking care that no air bubbles are entrapped underneath the prisms. The depth of solution to be observed on one side (usually the known solution) is arbitrarily set at a convenient number and the depth of the other side adjusted until the light transmitted through the two solutions is of equal intensity. A series of readings should be made and averaged to obtain the final result. This series should include an equal number of readings, deliberately starting with half of the field too dark in one instance and too light in the other, adjusting in only the one required direction in each instance until the match is obtained. This technique will eliminate any possible error due to eye adjustment. The formula: $c_2 = \frac{c_1 d_1}{d_2}$ is then used to calculate the concentration of the unknown solution, since $c_1$ is known and $d_1$ and $d_2$ may be read from the colorimeter.

**The Photoelectric Colorimeter.** The photoelectric colorimeter may be employed in the same situations as the visual colorimeter for the quantitative analysis of any liquid whose color intensity varies with the concentration of the unknown constituent. The inherent personal difficulties in the use of the visual colorimeter are eliminated. In addition, this instrument will evaluate, accurately and with ease, faint and difficult to measure colors.

The photoelectric colorimeter system, diagramed in Fig. 25, consists of a light source capable of emitting a beam of light of constant and definite intensity. This beam of light passes through a filter with proper transmission characteristics and then through an absorption cell containing the liquid under examination which absorbs a quantity of the light proportional to the color intensity of the liquid. The light transmitted by the liquid impinges on a photoelectric cell, initiating an electric current proportional to the intensity of the light hitting the cell, and the current developed is measured by a micro-ammeter. The entire system may be purchased in a compact unit from a number of supply houses or may be constructed in the laboratory without too much difficulty.[1]

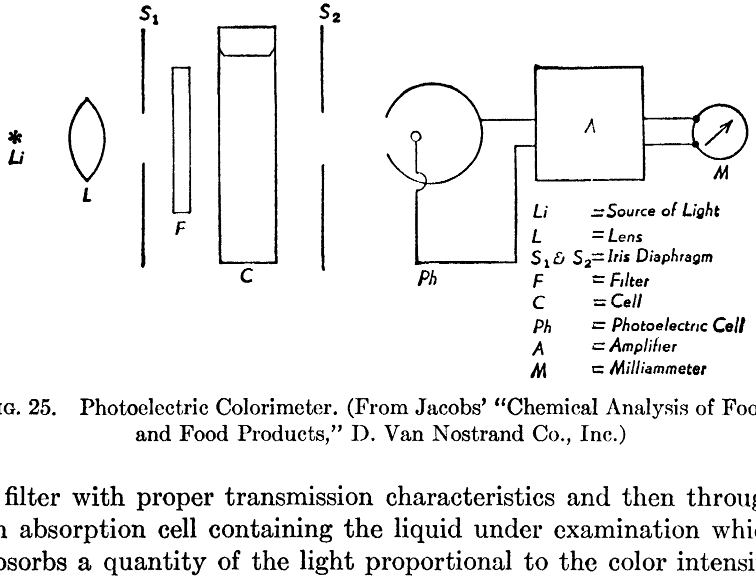

FIG. 25. Photoelectric Colorimeter. (From Jacobs' "Chemical Analysis of Foods and Food Products," D. Van Nostrand Co., Inc.)

*Procedure.* A calibration curve for a particular component is prepared by plotting readings on the instrument against the corresponding known concentration of the component in the solution. Once such a calibration curve covering a wide range in concentration has been established for a particular component, it is used to determine the concentration of the component in an unknown solution from the readings obtained on the instrument.

With slight modifications, the photoelectric colorimeter may be adapted to measure turbidity since variations in turbidity will affect the light transmitted to the photoelectric cell. Under these conditions, the instrument may be used as a turbidometer or a nephelometer. Since turibidity influences the amount of light transmitted by a solution, it is essential that no turbidity be present in a solution if its color concentration is to be determined accurately.

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[1] Frear, "Chemistry of Insecticides and Fungicides," D. Van Nostrand Co., Inc. (1942), p. 266.

Partridge, *Ind. Eng. Chem., Anal. Ed.*, **2**, 207, 1930; **3**, 169, 1931.

## SACCHARIMETRY

In sugar analysis it is necessary to be familiar with optical methods involving the polariscope and more particularly the saccharimeter.[1] These instruments make use of the fact that all the natural sugars possess asymmetric carbon atoms and consequently have the power of rotating the vibration plane of polarized light about an axis parallel to its direction of propagation. The angle through which this rotation occurs for substances in solution is directly proportional to the concentration of the substance, the length of the column of solution through which the light passes, and the rotating power of the substance.

The specific rotating power of a substance is termed its specific rotation and is taken as the unit of measurement of optical rotation. Specific rotation may be defined as the rotation in angular degrees of the plane of polarized monochromatic light which is produced by a solution of the optically active substance having a concentration of 1 gram in 1 ml. of solution and polarized in a column 1 dm. long. Ordinarily, sodium light or the *D* line of the spectrum is used as the monochromatic light source. Since temperature influences the rotating power of substances, readings are usually made and recorded at 20° C.

The complete expression of specific rotation is given by:

$$\frac{[\alpha]20^\circ}{D} = \frac{100\,a}{lc}$$

where

$[\alpha]20^\circ$ = specific rotation at 20° C. referred to the *D* line of the spectrum;

$a$ = observed angular rotation in degrees;

$l$ = length of column of solution in decimeters;

$c$ = concentration in grams per 100 ml.

[$c$ may be replaced by $pd$, where $p$ is the weight percentage or grams of solute in 100 grams of solution and $d$ is the density].

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[1] Browne and Zerban, "Sugar Analysis," John Wiley & Sons, Inc., 3d Ed. (1941).

Although the polariscope could be used in sugar analysis, the saccharimeter is more commonly employed. The essential differences between the polariscope and saccharimeter are that the polariscope employs monochromatic light and reads in angular degrees, whereas the saccharimeter uses white light and employs a quartz wedge compensation so that percentage of sugar may be read directly.

**Construction of the Saccharimeter.** The main parts of a saccharimeter assembly (diagramed in Fig. 26) consist of a light source from which light passes through a slit and a lens causing parallel light rays to be directed into the instrument. The light is plane polarized by passing through a Nicol prism (the polarizer) and then passed through the solution to be tested. The positive or negative rotation of the plane polarized light by the solution is compensated for by introducing sufficient positive or negative quartz wedges into the system to restore the balance. A scale attached to the quartz wedges is calibrated to read in percentage sugar. Another Nicol prism (the analyzer), a telescope, and a half-shadow field for obtaining the balance in rotation, complete the assembly.

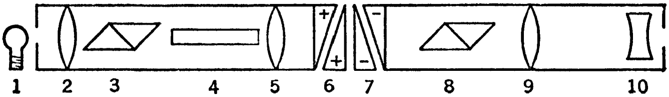

FIG. 26. Diagram of a Saccharimeter Assembly.

1. Light Source.
2. Lens.
3. Nicol Prism (Polarizer).
4. Sample Tube.
5. Lens.
6. Positive Quartz Wedge System.
7. Negative Quartz Wedge System.
8. Nicol Prism (Analyzer).
9. Lens.
10. Eyepiece.

The scale of the saccharimeter is so graduated that it reads into percentage of sugar directly, provided only one sugar is present, and provided also that a normal weight sugar sample has been polarized at 20° C. in a 200 mm. saccharimeter tube. A normal weight of sugar may be defined as that weight, which, when dissolved and diluted to a volume of 100 ml. at 20° C., and viewed in a 200 mm. tube at 20° C., will give a reading of 100° in the saccharimeter. The sugar scale originally adopted and used upon all German-made saccharimeters was that of Ventzke. With this scale, 26.048 grams of sucrose (weighed in air with brass weights) when dissolved in a volume of 100 Mohr cc. at 17.5° C., and polarized in a 200 mm. tube at 17.5° C. will give a reading of 100° on the saccharimeter. The International Sugar Commission, after considerable study, established a new sugar standard in 1900. According to their standard, a solution containing 26.000 grams of sucrose (normal weight) in 100 ml. of solution at 20° C., and polarized in a 200 mm. tube at 20° C. should give a reading of 100° on the saccharimeter. Since the scales on the German-made instruments have, in general, not been changed to conform to the new standards, a normal sugar solution prepared according to the International Sugar Commission requirements will give a reading of 99.9° instead of 100° on the saccharimeter. To eliminate this error without changing the scale necessitates correcting the normal weights of the various sugars so that they will give the correct reading. Thus, for sucrose, when using the old Ventzke scale, a weight of 26.026 grams (weighed in air with brass weights) dissolved in 100 ml. of solution at 20° C., and polarized in a 200 mm. tube at 20° C. will give a reading of 100° on the saccharimeter.

Normal weights of the various sugars when used with either of the two scales are as follows:

| *Sugar* | *Normal Weight* (International Sugar Commission) (grams) | *Normal Weight* (Corrected for use with old Ventzke scale) (grams) |
|---|---|---|
| Sucrose | 26.000 | 26.026 |
| Glucose | 32.366 | 32.398 |
| Fructose | 18.398 | 18.416 |
| Invert sugar | 86.247 | 86.333 |
| Lactose ($+H_2O$) | 32.939 | 32.972 |
| Maltose | 12.515 | 12.528 |
| Raffinose ($+5\ H_2O$) | 16.557 | 16.574 |
| Raffinose (anhydride) | 14.048 | 14.062 |

In order to be able to convert saccharimeter readings into polariscope readings, or vice versa, it is necessary to know the relationship existing between these instruments. When using the normal weights of sugars established by the International Sugar Commission, the following relationships hold: 1° International Sugar Commission Scale = 0.34620° Angular Rotation *D*, and 1° Angular Rotation *D* = 2.88850° International Sugar Commission Scale.

*Procedure.* The zero point of the instrument should be determined before its use in the analysis of sugar solutions. With the proper light and nothing in the barrel of the saccharimeter, set the one scale at zero and adjust the other scale until both fields viewed in the eyepiece are of the same light intensity. Under these conditions, the deviation from zero on the second scale will be the zero-point correction to be applied when using the instrument. Then place the clarified solution into a saccharimeter tube of the proper type, insuring that no air bubbles remain in the tube. Carefully wipe off the cover glasses on both ends of the tube and place the tube in the saccharimeter.

If the solution is dextro-rotatory, set the upper, or *K* scale, at zero and adjust the lower, or *A* scale, by turning the lower adjusting knob on the left side until both fields viewed through the eyepiece are of equal light intensity. If the solution is laevo-rotatory, the process is reversed by setting the lower or *A* scale at zero and obtaining the reading on the *K* scale.

It is advisable to make the readings in the following manner. After the one scale is set at zero adjust the other one until the one field is dark and the other light. Then move the adjusting knob in one direction only, until the two fields are of the same intensity and record the reading. Then deliberately turn the adjusting knob so that the field which was dark at the start, in making the first reading, is now the light field. Again by moving the adjusting knob in one direction only, establish a balance. Repeat this procedure until 3–5 readings have been obtained when starting from each side, and then average them to obtain the correct reading.

If it is necessary to control the temperature of the solution very accurately while making the reading, a jacketed saccharimeter tube should be employed. The most commonly used tubes are 200 and 400 mm. in length. The 400 mm. tube is used when the reading with the 200 mm. tube would be relatively small and so more difficult to read accurately. Shorter tubes for special determinations are available.

## HYDROGEN ION CONCENTRATION AND *p*H[1]

The two methods generally used for determining *p*H are the colorimetric and potentiometric methods. The latter is the more accurate method but there are times when a colorimetric or indicator method is to be preferred. Colorimetric determinations are usually reported only to the first decimal place of the *p*H, whereas potentiometric methods are read to the second decimal place in good work, and may be read to the third decimal place in research work. The potentiometric method is particularly useful with colored and turbid solutions. Furthermore, the method is used as a standard against which colorimetric apparatus should be checked occasionally and by which the results obtained colorimetrically are ultimately controlled.

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[1] The discussion under this topic was taken largely from Lisse's "Biocolloids"—Publisher, Edwards Bros. (1940), with the permission of the author.

**Colorimetric *p*H Methods.** The colorimetric method is based upon the principle that if an indicator is added to two different solutions and they assume the same shade of color, they have the same *p*H. The same shade of color means the same ratio of concentration of $\frac{\textit{acid form}}{\textit{alkaline form}}$ of the indicator. The determination consists in adding a measured volume of a suitable indicator to a certain volume of a solution, the *p*H of which is to be determined, and the color obtained compared with the color produced when the same indicator is added to buffer solutions of known *p*H in the La Motte method or with color discs in the Hellige method.

**La Motte Method.** It is first necessary to obtain a rough idea of the *p*H of the solution. Fill a tube from the Block Comparator Set to the 10 ml. graduation with the solution. By means of the graduated medicine dropper, add 0.5 ml. of 0.04 per cent bromothymol blue indicator to the solution and mix thoroughly. The color change for this indicator is from yellow at *p*H 6.0 on the acid side to deep blue at *p*H 7.6 on the alkaline side. At the neutral point it is greenish blue. Having determined whether the solution is acid, neutral, or alkaline, proceed with the other tests using the more acid or the more alkaline indicators, as the case may be, until the right indicator is found.

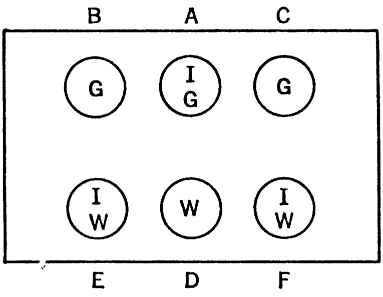

FIG. 27. Arrangement of Tubes when Using LaMotte Comparator. (Courtesy of LaMotte Chemical Products Co.)

Having found the proper indicator to use, fill three clean test tubes to the 10 ml. mark with the liquid to be tested and place them in the holes marked *B*, *A*, and *C* (Fig. 27). Tubes *B* and *C* correct for any effects of color or turbidity in the liquid being tested. To the middle tube *A* add 0.5 ml. of the proper indicator solution, by means of the medicine dropper, and mix the contents thoroughly. Place the tube of distilled water from the set in the hole marked *D*, and two of the color standards, differing by only 0.2 *p*H, in the holes *E* and *F*. Look through the three pairs of tubes, holding them toward a window or Daylight Lamp, with the etched glass on the side facing the source of light and change the color standards until the central pair of tubes exactly matches one of the other pairs, or until the color of the central pair lies between the colors of the pairs on both sides. If an exact match is obtained, the *p*H of the solution is read off directly from the standard with which the match is obtained. If the color of the central pair of tubes lies between the colors of the pairs on both sides, the *p*H value is taken as the average of the two.

The ranges of the various indicators available for the determination overlap each other. Thus, when a *p*H value falls in such an overlapping range, it is advisable to make determinations with both indicators since there are instances in which indicators do not indicate the correct *p*H, especially near the end of their range. If results obtained with overlapping indicators do not agree, one should check the values potentiometrically.

Each tube in a Comparator set contains a buffer solution of the *p*H indicated with added indicator. Since indicators are unstable to light and heat, they should be kept in the dark in the refrigerator when not in use. A Comparator set, especially if old or if used and exposed for much time, should be tested against potentiometrically determined solutions to ascertain if the *p*H value given on the indicator vials is accurate.

**Hellige Method.** This method substitutes nonfading colored-glass standards in the form of discs for the colored buffer solutions used in the La Motte Comparator. Each disc[1] covers an indicator range. A range finding disc, covering *p*H 3–11, is useful for quickly finding the proper disc and indicator to use. One can use the method starting with bromothymol blue as in the La Motte method, to detect what indicator and disc to use.

If the test solution is colorless, or only slightly colored, it can be used directly for the *p*H test. Solutions having much color or turbidity must be diluted with distilled water or a solution of sodium chloride of approximately the same salt content as the test solution. Special precautions are necessary in diluting unbuffered solutions, especially when their *p*H is near the neutral point. However, buffered solutions can be diluted many times without affecting the *p*H value until the color or turbidity is sufficiently eliminated to obtain satisfactory results.

The color disc for the indicator to be used is placed into the Comparator housing. This is done by opening the front cover of the housing and placing the center of the color disc on the ring in such a way that the number plates of the disc face the worker; then close the front cover of the housing.

[1] Two types of color discs are now available; one type for daylight and another for artificial illumination.

The solution to be tested, properly prepared, is poured into one of the graduated test tubes and filled to the 5 or 10 ml. mark. A quantity of indicator solution of the dilute form in the proportion specified on the label of each color disc box is added and the solution well mixed. This test tube with its contents is placed in the right-hand opening of the Comparator. A quantity of test solution without the addition of indicator is poured into the other tube and placed in the left-hand opening. This test solution serves to balance the color fields and eliminates any errors due to the original color or turbidity of the test solution. The color comparison is made by turning the color disc until the color of the test solution matches one of the color glass standards of the color disc, or lies between two adjacent standards. In this position the *p*H value is read directly from a figure appearing either through the upper or lower hole in the front cover of the apparatus. Errors in reading are impossible since the figure showing the result appears only in the upper or lower hole. If the match of color is not exact, interpolation permits a reading with an accuracy of at least 0.1 *p*H. It is advisable to make all tests at approximately the same temperature.

**Potentiometric Methods.** If a metal is placed in a solution of one of its salts, the atoms of the metal tend to become ionic, a tendency which is opposed by the osmotic pressure of the ions. The solution, as well as the metal, is electrically neutral of itself. If the metallic atoms become ions, the atoms of the metal will leave behind them negative charges (electrons) on the electrode, the solution becoming positively charged; if the metallic ions become metallic atoms, the ions will take on negative charges from the electrodes and the electrode will become positively charged. In either instance, a difference in potential, measured by voltage, is set up. The extent of this difference of potential is dependent on the concentration of the ion of which the electrode is composed and is given by the equation:

$$P = P_M + \frac{0.0001983\ T}{n} \log \frac{1}{C}$$

where $P$ = potential in volts;
$P_M$ = standard electrode potential in volts;
$T$ = absolute temperature;
$n$ = valence;
$C$ = concentration of the ion in terms of $M$.

In the event that the electrode is a hydrogen electrode, the potential of which is dependent on $[H^+]$, $n$ becomes 1. If the temperature is 25° C. (298° abs.), the equation becomes:

$$P = P_M + 0.0591 \log \frac{1}{C}.$$

A single electrode is not sufficient for measuring the value of $P$ since the electrical circuit must be completed. The potential of two electrodes of the same element, in solutions of two different concentrations of the ion of that element, can be compared even though the absolute value of neither one is known. The difference in the two potentials produces a voltage which varies with the ratio of the two concentrations in such a manner that, if the voltage is measured and the concentration in contact with one electrode is known, the other can be determined. This follows from the derivation:

$$P_1 - P_2 = \left(P_M + 0.0591 \log \frac{1}{C_1}\right) - \left(P_M + 0.0591 \log \frac{1}{C_2}\right)$$

$$P_1 - P_2 = P_M + 0.0591 \log \frac{1}{C_1} - P_M - 0.0591 \log \frac{1}{C_2}$$

$$V = 0.0591 \log \frac{C_2}{C_1}$$

in which $P_1 - P_2$, the difference in potential, equals the voltage, $V$. If $C_2 = 1M$, then the equation becomes

$$V = 0.0591 \log \frac{1}{C_1} = 0.0591 \log \frac{1}{[\mathrm{H}^+]\ \text{unknown}}$$

and $V = 0.0591\ p\mathrm{H}$ at 25° C. This equation indicates that voltage and $p$H are proportional to each other.

The above equation is a derivation of the Nernst equation as usually written:

$$V = \frac{RT}{nF} \ln \frac{C_2}{C_1}$$

where $R$ = the gas constant in volt-coulombs = 8.315;
$T$ = absolute temperature, which at 25° C. = 298;
$n$ = valence = 1 for the hydrogen electrode;
$F$ = Faraday = 96,500 coulombs;
ln = natural logarithm, which can be changed to $\log_{10}$ or log, by multiplying by 2.3026, a constant ($K$).

Accordingly $\frac{RT}{nF} K = \frac{8.315 \times 298 \times 2.3026}{1 \times 96{,}500} = 0.0591.$

The hydrogen ion concentration of an aqueous solution may be determined by the use of two hydrogen electrodes connected by an agar-neutral salt bridge (Fig. 28) and the voltage read by a potentiometer. Upon substitution of the voltage reading in the foregoing equation, the *p*H of the aqueous solution may be calculated.

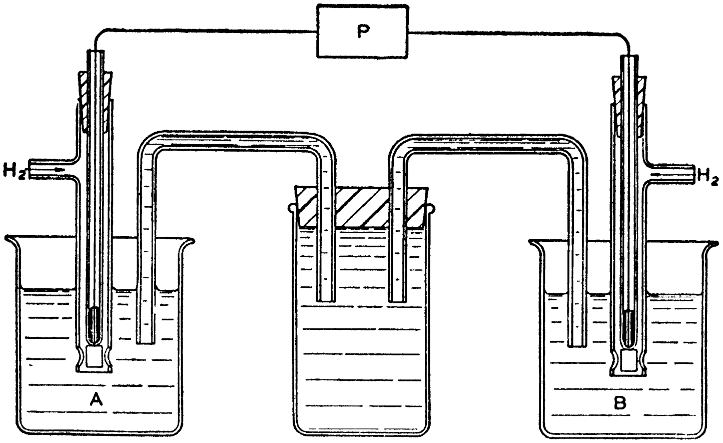

FIG. 28. Hydrogen Ion Concentration Chain.
(Courtesy of Leeds and Northrup Co.)

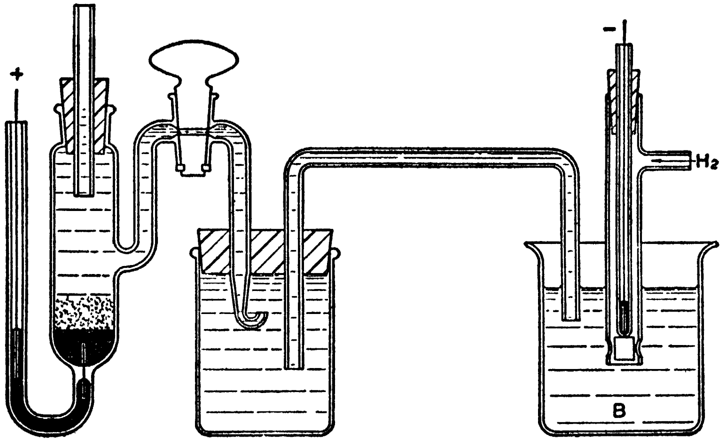

FIG. 29. Practical Hydrogen Ion Concentration Chain.
(Courtesy of Leeds and Northrup Co.)

In order to use the set up given in Fig. 28, solution *A* must be exactly *N*. This can be accomplished by the use of buffered solutions which must be checked regularly. A much more convenient arrangement (Fig. 29) is one in which a calomel electrode replaces the N hydrogen electrode. This is preferable because it is easy to keep a calomel electrode at a definite potential, whereas a variation of the hydrogen ion concentration of a N hydrogen electrode would produce a change in potential. Since a calomel electrode has been substituted for a N hydrogen electrode, the difference in voltage between the calomel electrode and the normal hydrogen electrode ($v$) must be inserted into the above equation. The equation then becomes,

$$V - v = 0.0591\ p\text{H}.$$

There are four types of calomel electrodes: 0.1 N, 1 N, 3.5 N, and saturated. The value of $v$ depends upon the type of calomel electrode and on its temperature, as shown in Table 10.

TABLE 10. VALUES OF $v$ FOR CALOMEL ELECTRODES

| Type | $v$ at 20° C. | $v$ at 25° C. | $v$ at 30° C. |
|---|---|---|---|
| 0.1 N | 0.3379 | 0.3376 | 0.3371 |
| 1.0 N | 0.2860 | 0.2848 | 0.2835 |
| 3.5 N | — | 0.2522 | — |
| Saturated | 0.2496 | 0.2458 | 0.2420 |

The saturated calomel electrode is most commonly used because it is more easily prepared and its potential is less subject to change in concentration than the others. It is, however, affected to a greater degree by a change in temperature (Table 10) and hence temperature conditions must be observed more strictly than when the others are used. A diagram of the calomel electrode is given in Fig. 30.

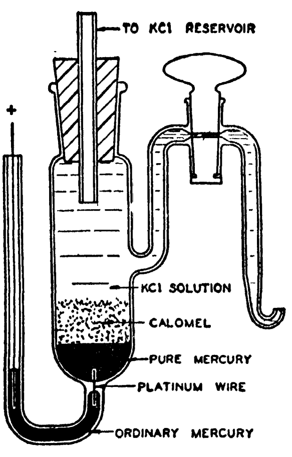

FIG. 30. Elements of a Calomel Electrode. (Courtesy of Leeds and Northrup Co.)

The salt bridge consists of 3 per cent agar saturated with potassium chloride. The connecting vessel is filled with saturated potassium chloride solution. A contact potential, which can arise at the junction where two solutions of different composition come into contact, is eliminated since the $K^+$ and $Cl^-$ move at about the same rate (comparable transport numbers). The use of a potassium chloride-agar bridge, then, gives a contact potential whose value is approximately zero and so, for practical purposes, may be neglected.

A *hydrogen electrode* usually consists of platinum or gold, coated with a layer of platinum black. It is made to absorb hydrogen gas to saturation, and is immersed in the solution whose [$H^+$] is to be determined, developing there a potential which is a function of the [$H^+$]. When platinized, it catalyzes the equilibrium reaction between hydrogen molecules and atoms and accelerates the equilibrium which must be obtained between these atoms and hydrogen ions in order to produce the definite potential which is dependent on the $H^+$ concentration.

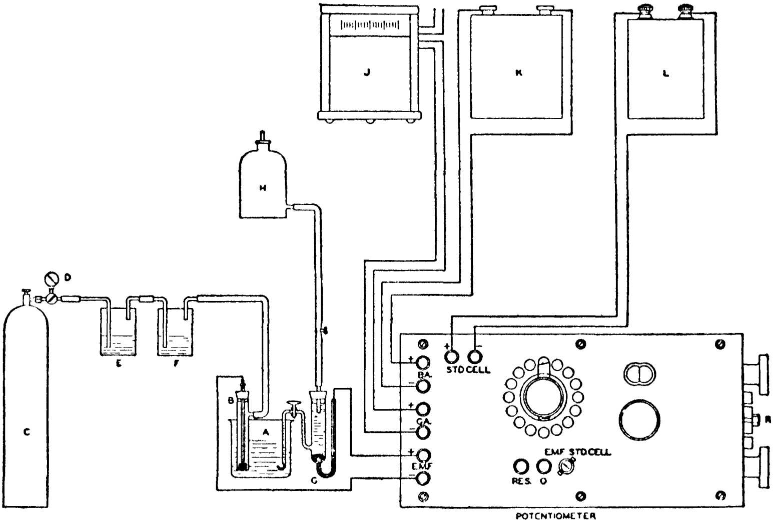

FIG. 31. Scheme of Assembly for Hydrogen Ion Measurements. (Courtesy of Leeds and Northrup Co.)

A.—Sample to be tested for pH.
B.—Bubbling hydrogen electrode.
C.—Hydrogen cylinder.
D.—Pressure reducing valve.
E. and F.—Purifying solutions (to purify the hydrogen gas).
G.—Calomel electrode.
H.—Reservoir of KCl (saturated with calomel) for flushing calomel electrode.
J.—Galvanometer.
K.—Working batteries.
L.—Standard cell.
R.—Resistance.

The determination of the hydrogen ion concentration from the difference of potential between the two half cells requires the voltage to be measured under a condition in which no appreciable current is allowed to flow, since voltage changes with flowing current. A voltmeter cannot be used, because it requires a current to actuate it. A potentiometer is an ideal instrument to use, since, when the unknown E.M.F. is balanced by an opposed but known E.M.F., no current will flow through the cell. This is indicated by a null-point instrument, such as a galvanometer.

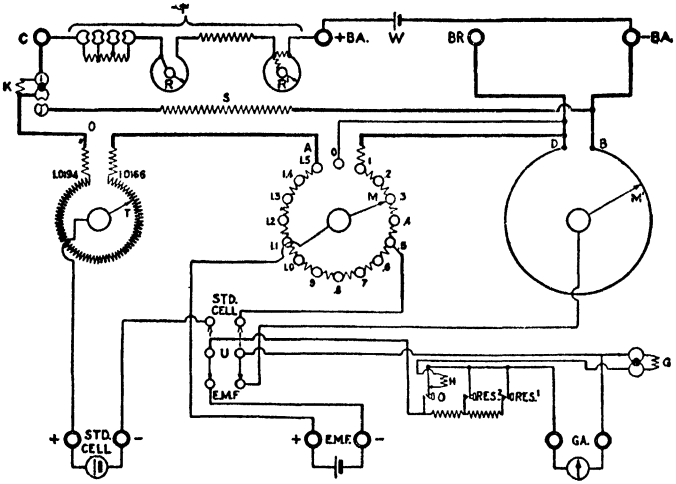

FIG. 32. Scheme of a Potentiometer Circuit for Measurements of High Precision. (Courtesy of Leeds and Northrup Co.)

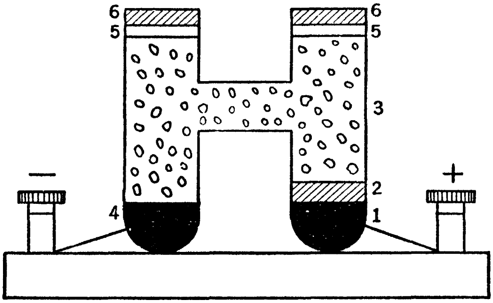

FIG. 33. Diagram of a Standard Cell.

1. Mercury.
2. Cadmium Sulfate-Mercurous Sulfate Paste.
3. Saturated Cadmium Sulfate Solution Containing Crystals of Cadmium Sulfate.
4. Cadmium Amalgam.
5. Paraffin.
6. Cork.

A complete assembly for hydrogen ion measurement is given in Fig. 31. The scheme of a potentiometric circuit is given in Fig. 32.

The *standard cell* gives a constant and perfectly definite E.M.F. It is a so-called *Cadmium cell* or *Weston cell,* the necessary parts of which are pictured in Fig. 33. Essentially it consists of two half cells: Hg in contact with $Hg^+$ of a concentration found in saturated mercurous sulfate (+ pole), and cadmium amalgam in contact with $Cd^{++}$ of a concentration found in saturated cadmium sulfate at room temperature, or in a saturated solution at 4° C. (− pole). Since the ion concentrations remain constant, one would expect such a cell to have a definite voltage. When properly constructed it gives a constant E.M.F. of 1.0183 volts at 20° C., which should remain unaltered for years if not short circuited. Its temperature coefficient is extremely small. This cell is not intended for use as a source of current. Its only value is its reliability as a standard of voltage for standardizing the potentiometer circuit.

*Procedure with the Hydrogen Electrode.* Compare the voltage of the potentiometer circuit with that of the standard cell by closing the switch that puts the standard cell and the working battery in circuit, tap the galvanometer keys (Res. and 0, Fig. 31) lightly, and note the deflection of the galvanometer. The amount and direction of the deflection indicates the adjustment required in the rheostat (*R*, Fig. 31) for controlling the current in the measuring circuit. Change the setting of *R* until the galvanometer index does not move when the most sensitive key is closed and opened. So long as the deflection is appreciable, tap but do not press the keys, but when the deflection is near zero, the key can be held down while final adjustment of the rheostat is made. The voltage of the potentiometer circuit is now properly adjusted. Next throw the switch to put the electrodes in circuit in place of the standard cell, tap the galvanometer keys, and adjust the dial switch (which reads to 0.1 volt) and the slide-wire (which reads to as low as 0.01 millivolt). When there is no deflection of the galvanometer as the most sensitive key is pressed and released, the voltage produced by the electrodes is exactly balanced against the potentiometer voltage. Then the switch and slide-wire settings give the value of the electrode voltage, which, when substituted in the proper equation, gives the *p*H. It is wise to check again the potentiometer voltage against the standard cell as explained above, and, if there is any deflection of the galvanometer, to make the necessary adjustment of the rheostat to bring the deflection to zero, and then to repeat the measurement with the dial switch and slide-wire (having thrown the electrodes into circuit). At 25° C., the following equations can be used:

For the saturated electrode, $p\text{H} = 16.9 \times (V - 0.2458)$
For the normal electrode, $p\text{H} = 16.9 \times (V - 0.2848)$
For the 0.1 normal electrode, $p\text{H} = 16.9 \times (V - 0.3376)$

where $V$ is the voltage measured; $16.9 = \frac{1}{0.0591}$; and the other values are the potentials given in Table 10.

To check the hydrogen electrodes that have been platinized and the potentiometer system as a whole, a solution whose *p*H is accurately known (standard buffer solution prepared or purchased for this purpose) is tested. Determine whether the voltage reading which should be given according to formula is given within the limit of accuracy of the most sensitive buffer solution. If the system gives the required voltage of the standard buffer solution, it is in proper condition for *p*H measurements. A drift in potential indicates that probably a hydrogen electrode is not functioning properly and should be replatinized or completely saturated.

*The Quinhydrone Electrode.* This electrode has an advantage over the hydrogen electrode in that it need not be platinized nor supplied with hydrogen gas. It consists of a smooth piece of platinum or gold which is dipped into the solution to which quinhydrone is then added. Quinhydrone dissociates into quinone and hydroquinone. The quinhydrone can be prepared by mixing solutions of pure quinone and hydroquinone in equimolecular ratio.

The quinhydrone electrode is an oxidation-reduction electrode. The reaction taking place at the electrode is:

$$\underset{\text{Oxidant}}{\overset{\text{Quinone}}{C_6H_4O_2}} + 2\,H^+ + 2\,\epsilon \rightleftarrows \underset{\text{Reductant}}{\overset{\text{Hydroquinone}}{C_6H_6O_2}}$$

The potential obtained when using this electrode is dependent on the hydrogen ion concentration as shown by the equation: (At 25° C.)

$$E = E_0 + \frac{0.0591}{2} \log \frac{[\text{Quinone}]}{[\text{Hydroquinone}]} + 0.0591 \log [H^+].$$

However, since the ratio of the concentrations of quinone and hydroquinone when added is 1, and the log of 1 is zero, the potential is related to the $[H^+]$ according to the simpler equation:

$$E = E_0 + 0.0591 \log [H^+]$$

where $E_0$ is the normal potential of the quinhydrone electrode referred to the normal hydrogen electrode, and has a value of 0.699. When the saturated calomel electrode, which has a value of 0.246 at 25° C., is used, and when we consider that the potential of the quinhydrone electrode is positive to that of the hydrogen electrode, the equation becomes:

$$\begin{aligned}
E &= E_0 - 0.246 + 0.0591 \log [\mathrm{H}^+] \text{ at } 25^\circ \text{ C.} \\
E &= 0.699 - 0.246 + 0.591 \log [\mathrm{H}^+] \\
E - 0.453 &= 0.0591 \log [\mathrm{H}^+] \\
0.453 - E &= -0.0591 \log [\mathrm{H}^+] \\
\frac{0.453 - E}{0.0591} &= p\mathrm{H}.
\end{aligned}$$

We note that another factor was introduced into the equation; it was the difference in value between the potential obtained with a hydrogen electrode and that obtained with the quinhydrone electrode.

When the saturated calomel and quinhydrone electrodes are used with an ordinary potentiometer, the calomel electrode must be connected to the negative binding post and the quinhydrone electrode to the other post (E.M.F.), when measuring any solution whose *p*H is less than 7.67 at 25° C. This is a connection, the reverse of that described under hydrogen electrodes. If solutions of a *p*H greater than 7.67 are measured, the connections must be the reverse of that just stated, i. e., must be as when using hydrogen electrodes. A special potentiometer designed for quinhydrone work takes care of the reversal of binding posts (when used below *p*H 7.67) in its construction. Quinhydrone electrodes are not satisfactory in solutions more alkaline than *p*H 8 or 9.

Measurements are made as with the hydrogen electrode except that no hydrogen is passed into the solution. Instead enough quinhydrone is added to saturate the solution (50–100 mg. per 20 ml.) and the electrode is inserted. The mixture is shaken for about one minute and voltage readings are made. Substitution in the proper formula enables one to calculate the *p*H.

*The Glass Electrode.* In general, this instrument permits accurate measurement of *p*H from 1 to 9 even in the presence of oxidizing-reducing agents, colloidal matter, etc., in unbuffered solutions, and in semi-solid and plastic materials. Above *p*H 9 corrections must be made, especially for high concentrations of sodium ions. However, a special electrode has been developed and is available to measure *p*H values above 9.0 in the presence of a high concentration of sodium ions. No foreign substance is added to the solution. For these reasons and because of its inertness toward chemical reaction with components of the test material, the glass electrode is finding wide application.

In the glass electrode, a glass surface of the proper composition has the property of generating across its surface an electrical potential whose magnitude is directly proportional to the *p*H of the solution. But since the current is very slight, because of high resistance across the glass, a supersensitive null-point instrument (quadrant electrometer) must be used to measure the E.M.F., or the current must be amplified by the use of vacuum tubes.

Since the various commercial instruments available for measuring *p*H with the glass electrode vary somewhat in their design, the reader is referred to the instructions accompanying each type of instrument for the exact method of operating it. The basic principles of hydrogen-ion determination discussed previously will be found helpful in understanding the principle and operation of the glass electrode.

## CONDUCTIVITY[1]

The conductivity of an electrolyte is not measured directly but is determined from a measurement of the resistance of the solution between two electrodes immersed in it. The reciprocal of the measured resistance is the conductance of the solution. The resistance of the solution is commonly measured by the alternating current Wheatstone bridge method. The essential features of an equipment for measuring the resistance of an electrolyte by this method are indicated in Fig. 34.

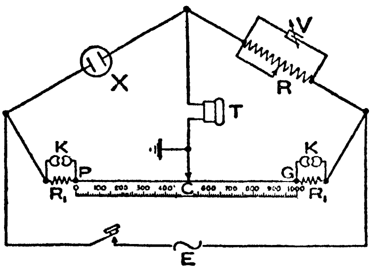

FIG. 34. Diagram of Set-up for Measuring Electrolytic Resistance. (Courtesy of Leeds and Northrup Co.)

In this diagram, *X* represents a conductivity cell, with the two electrodes immersed in the solution, connected in one arm of the bridge circuit. In an adjacent arm is a variable resistance *R*. The other two arms of the bridge consist of a wire *PG*, with a sliding contact *C*, which provides a variable ratio. A source of alternating current for the bridge circuit is indicated at *E*, and *T* represents a telephone to detect when the bridge is in balance.

**Procedure.** In making a measurement, the contact *C* is moved along the wire until there is silence or a minimum of sound in the telephone. If the slide wire is uniform in character, the resistance of the section on either side of the contact will be proportional to its length. With a scale of 1000 divisions from $P$ to $G$, if $A$ represents the scale reading for the contact when the bridge is balanced, and $R$ the setting of the variable resistance, the resistance of the solution between the electrodes may be found from the equation:

---

[1] The following information is taken largely from Leeds and Northrup, *Catalog No. 48.*

$$X = R\left(\frac{A}{1000-A}\right).$$

The specific conductance or conductivity is defined as the conductance of 1 cm. cube of the material. Therefore, if the electrodes of the conductivity cell are not exactly 1 sq. cm. in area and 1 cm. distant from each other, the measured resistance or conductance of the solution placed between them will have to be multiplied by a factor to convert the value to that which would be obtained if the electrodes enclosed between them 1 cm. cube of the solution. This factor, also known as the *cell constant,* depends on the size and shape of the electrodes and on their distance apart. If $C$ is the specific conductance and $c$ the measured conductance, $K$, the cell constant will be: $K = C/c$.

The cell constant can be determined readily by measuring the conductance of a solution of known conductivity, such as a 0.002 N potassium chloride solution. The conductivity of this solution, expressed in mhos, is given in Table 11.

TABLE 11. CONDUCTIVITY IN MHOS OF 0.002 N KCl SOLUTION

| Temperature °C. | Conductivity |
|---|---|
| 10 | $1.996 \times 10^{-3}$ |
| 20 | $2.502 \times 10^{-3}$ |
| 25 | $2.768 \times 10^{-3}$ |

## VISCOSITY

Matter which will deform permanently, to an extent directly proportional to the deforming force applied, is said to be viscous. Viscosity can be defined as the resistance due to internal friction which viscous matter offers to deforming forces, hence, as resistance to shear or flow.

When viscous matter fills the space between two parallel planes a distance $S$ apart, the tangential force $F$, required to maintain a rate of flow $V$ of one plane with respect to the other, will cause a rate of shear equal to $V/S$ throughout the matter. The ratio of the force $F$ (equal to that caused by the internal friction of the matter) to the rate of shear is called the coefficient of viscosity (eta, $\eta$). Accordingly: $\eta = FS/V$.

The absolute unit of viscosity is the poise. In c.g.s. units, a poise is the force which, when exerted on a unit area between two parallel planes one square centimeter in area and one centimeter apart, produces a difference in the velocity of streaming between the two planes of one centimeter per second. A centipoise is one one-hundredth poise.

It has been customary and convenient to determine relative viscosity rather than absolute viscosity. Relative viscosity expresses viscosity in terms of some standard such as water, whose absolute viscosity at 20° C. is 1.0050 centipoises. Accordingly, the relative and absolute viscosity are practically identical when expressed in centipoises.

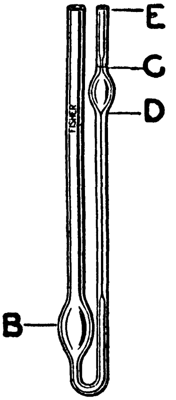

Fig. 35. Ostwald Viscosity Pipette. (Courtesy of Fisher Scientific Co.)

**Ostwald Viscometer** (Fig. 35). This instrument consists of a **U**-shaped tube with a small bulb emptying into a capillary in one arm, joined to a much wider tube containing a bulb. A properly shaped piece of cork inserted between the two arms of the viscometer gives support to the instrument and so prevents it from being easily broken. It is essential that the capillary of the viscometer be absolutely clean. To insure this, wash with warm cleaning solution, rinse with plenty of water, then with alcohol and ether, and dry with a current of warm air freed from dust by passing through glass wool. Obviously, since viscosity depends upon the head and the temperature, the viscometer should be suspended vertically in a constant temperature bath consisting of a large glass beaker holding at least three liters of water, or in a thermostat, constant within 0.1° C.

When a certain volume of the liquid has been introduced into the left-hand arm it is drawn into the right-hand arm above the line at $C$ by sucking on the rubber tube attached at $E$. Sufficient liquid is that quantity which leaves some in the bulb $B$ when the right-hand arm has been filled to above $C$. The time interval between the time that the surface of the liquid passes $C$ and $D$ is taken with the aid of a stop watch.

The viscosity is given by equations based on the flow of a liquid through a capillary. Theoretically, such a column of liquid is composed of innumerable concentric cylinders, each moving slightly faster than its neighbor as the distance of the circumference of the cylinder from the wall of the tube is increased.

The modification of Poiseuille's formula by Stokes and Hagenbach is generally accepted as applicable to truly viscous flow:

$$\eta = \frac{\pi\, r^4 pt}{8\chi v}$$

where $\eta$ = coefficient of viscosity;
$r$ = radius of the capillary tube;
$p$ = driving force of the liquid flowing through the tube;
$t$ = time necessary for the volume ($v$) to flow through the capillary;
$\chi$ = length of the capillary.

$$p \text{ (the driving force)} = hdg,$$

where $h$ = average difference in level of the liquid in the two arms of the viscometer;
$d$ = density of the liquid;
$g$ = acceleration of gravity.

Having made the viscosity readings for the liquid, clean the instrument and pipette into it the same volume of water as was used above for the liquid. Under such conditions $\pi$, $r$, 8, $\chi$, and $v$ are constants. Then using subscript (1) for the liquid and (0) for the water,

relative viscosity $\frac{\eta_1}{\eta_0} = \frac{p_1 t_1}{p_0 t_0}.$

Substituting ($hdg$), the driving force for ($p$), the equation becomes

$$\frac{\eta_1}{\eta_0} = \frac{hd_1gt_1}{hd_0gt_0} = \frac{d_1t_1}{d_0t_0}.$$

Hence, it is apparent that the relative viscosity ($\eta_1/\eta_0$) is a function of the densities and times of outflow of the two liquids used, provided the same viscometer and the same volume are used for both time readings. The absolute viscosity can be obtained by substituting the c.g.s. value of the viscosity of the water for $\eta_0$. The densities can be determined by means of a pycnometer. This must be done at the temperature at which the viscosity was determined.

The capillary tube of the viscometer has a bore of 0.4 to 0.6 mm. and a length of about 6 cm. There is a critical capillary radius and length above which radius, and below which length, viscosity measurements in the Ostwald viscometer no longer yield accurate results. With such a bore, viscosities up to twenty-five times that of water can be measured. For higher viscosities, the bore can be increased or a torsion type of instrument can be used. The foregoing equation does not hold if the diameter of the bore is decreased greatly.

The material of which capillary viscometers are made (usually glass) has no effect because there is a thin film of liquid adsorbed on the inner wall of the capillary tube; consequently there is no friction between the wall of the tube and the liquid, but all the internal friction is between liquid and liquid. An ordinary pipette, especially if its tip is drawn out sufficiently small, is suitable for rough comparative measurements, in which the time of outflow between marks above and below the bulb gives a relative measure of the viscosity.

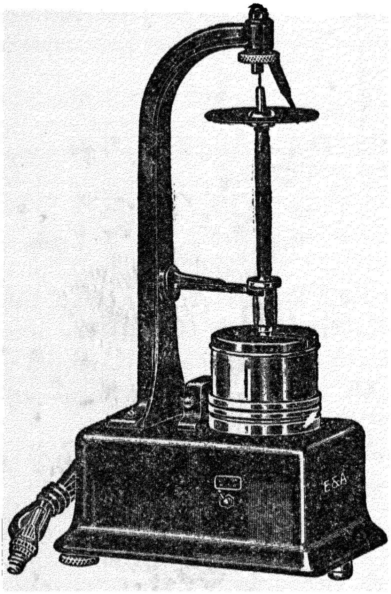

FIG. 36. MacMichael Viscosimeter. (Courtesy of Fisher Scientific Co.)

**The MacMichael Torsion Viscometer.** This viscometer determines a wide range of viscosities, from viscosities a little above that of water to those of thick glues. Results are accurate and are not affected by the specific gravity of the material. This viscometer is especially useful in the study of viscous materials which could not be tested in the Ostwald type of viscometer. The MacMichael instrument is used in determining the viscosity of varnishes, greases, flours, gelatins, ice cream mixes, glues, starches, chocolate and cocoa solution, paints, oils, dyes, sugar solutions, etc.

[1] The MacMichael (Fig. 36) operates on the torsion principle. A plunger of standard dimensions is suspended by a torsion wire of exact length from the top of the instrument. The material is placed in a cup which is revolved at a constant rate of speed on a motor driven platform. The amount of twist imparted to the wire, depending upon the viscosity of the material, is read on a graduated

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[1] The following information is taken from Eimer and Amend *Bul. 400.*

disc. The disc is attached to a spindle, at the bottom of which the plunger is fastened. The graduations on the disc are in degrees MacMichael (1/300 circle). The angular twist given to the plunger by the rotating liquid causes the hollow spindle to turn around the wire as an axis, carrying with it the disc through a certain number of divisions which can be read directly under the tip of the adjustable pointer and which indicate the pull of the rotating liquid that surrounds the plunger. By standardizing against solutions of known viscosity in poises, the results can be interpreted in poises, i. e., absolute units of viscosity.

The cup which holds the sample is placed within an outer cup which serves as a water or oil bath for heating the material if desired. The outer cup has an enclosed electric heating unit, the inner bottom of the cup being rounded so that it is readily cleaned. The desired temperature is maintained by means of a sliding contact against the rim near the bottom of the cup, so that the material may be heated while the cup revolves.

A disc plunger is used in conjunction with the large inner cup. A small cup, 3 cm. in diameter, which fits the large inner cup by means of a bayonet lock, is also supplied. A cylindrical plunger, 1 cm. in diameter, for use with the small inner cup, is employed mainly for testing liquids for high viscosity, or when only small quantities of material are available.

# PART V

# GENERAL METHODS USED IN AGRICULTURAL AND FOOD ANALYSIS

## CHAPTER X

## GENERAL METHODS

### ANALYSIS FOR PROTEIN CONTENT

The analysis of a compound for its protein content by the Kjeldahl method is based upon the determination of the amount of reduced nitrogen present—that is, its $-NH_2$ and $=NH$ nitrogen. Ammonium compounds, urea, amino acids, and more complex breakdown products of proteins will also be determined as protein unless removed previous to the analysis. An excellent review of the Kjeldahl determination of organic nitrogen is given by Bradstreet.[1]

**Kjeldahl Method.** The Kjeldahl method as modified by Gunning and Arnold, consists of: first, the wet oxidation of the sample and the conversion of protein nitrogen into ammonium sulfate; second, the decomposition of the ammonium sulfate with strong alkali and the distillation of the ammonia evolved into standard acid; third, the titration of the standard acid with standard base; and fourth, the calculation of the percentage protein in the sample from its weight and the volume of standard acid neutralized by the ammonia.

A blank is run through the entire process with the samples. The blank corrects for the amount of ammonia derived from the reagents, containing as they may, traces of ammonium compounds or nitrates which can be reduced to ammonia in the process. The same reagents in the same proportions are used as in the sample determination and only the sample itself is omitted. If a piece of filter paper was used to wrap the sample, a similar piece of filter paper is added to the blank. If no paper was used, add to the blank a piece of filter paper or a lump of sugar to create a reducing condition similar to that which obtains in the sample where organic matter is present.

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[1] Bradstreet, *Chem. Rev.*, **27**, 331 (1940).

A Kjeldahl digestion and distillation apparatus (Fig. 37) speeds up and simplifies the determination considerably, although such an elaborate apparatus is not essential. The digestion may be conducted over a flame in a hood while the distillation may utilize only a trap and condenser. A satisfactory simple arrangement is to connect the digestion flask to a water pump (Fig. 38) which conducts the fumes into the water and so down the drain. With this set up several samples may be digested simultaneously in the laboratory without suffering any inconvenience from the fumes produced in the flasks.[1]

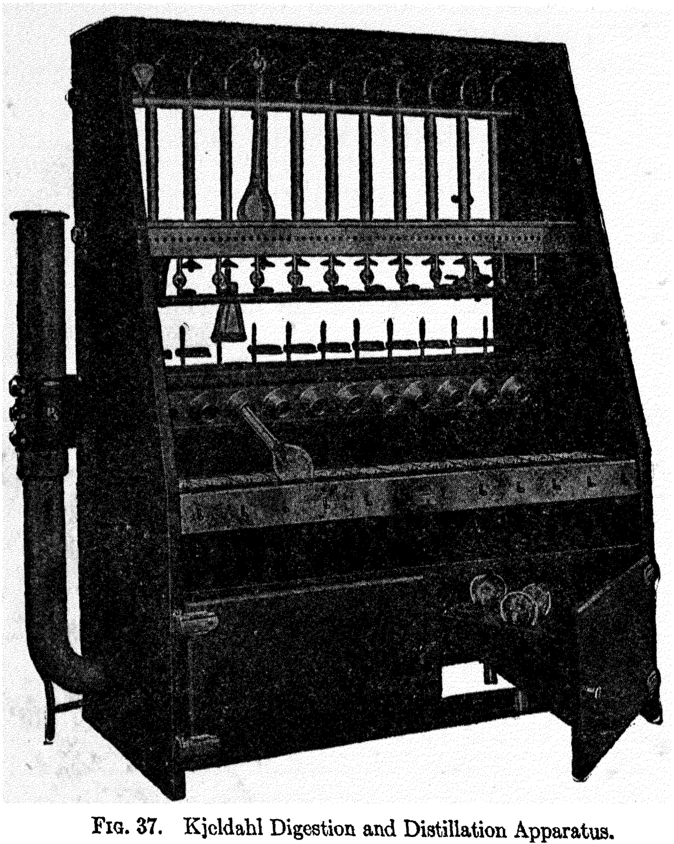

FIG. 37. Kjeldahl Digestion and Distillation Apparatus. (Courtesy of Burrell Technical Supply Co.)

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[1] Sy, *Ind. Eng. Chem.*, 4, 680 (1912).

*Reagents.*

1. *Standard 0.1 N sulfuric acid solution.*
2. *Standard 0.1 N sodium hydroxide solution.*
3. *Kjeldahl alkali solution* prepared by dissolving 500 grams of technical grade sodium hydroxide, free from nitrates, in water and diluting to 1 liter of solution.
4. *Mixed methyl red or methyl red indicator solution* (see p. 72).

*Oxidation Process.* The wet oxidation of the sample is accomplished by heating with concentrated sulfuric acid in the presence of an oxidizing catalyst and a salt, either potassium or sodium sulfate.

A sample weight of 0.7–3.5 grams, depending upon the nitrogen content, is called for in the general Kjeldahl method. Usually a sufficient weight of sample is taken so that the ammonia distilled will neutralize from 15–25 ml. of 0.1 N acid in the receiving flask. If the sample is a solid, it may be wrapped in filter paper to prevent any of the sample from sticking to the neck of the Kjeldahl flask when it is introduced into the flask.

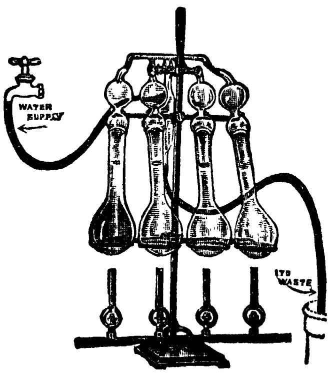

FIG. 38. Sy Kjeldahl Digestion Apparatus. (Courtesy of Fisher Scientific Co.)

Twenty to thirty milliliters of concentrated sulfuric acid are added to oxidize the organic matter and combine with the ammonia produced. In the oxidation, the carbon and hydrogen are converted to carbon dioxide and water. A portion of the sulfuric acid is reduced in the process to sulfur dioxide. This agent is responsible for reducing the nitrogenous compounds to ammonia which, in turn, reacts with the sulfuric acid to form ammonium sulfate. Enough sulfuric acid must be added also to provide sufficient solution in the flask. The volume of liquid in the flask throughout the digestion process should be kept above 10 ml. and if it becomes less, more concentrated sulfuric acid should be added. The amount of acid required to digest 1 gram of organic matter varies with the type of material being oxidized. For complete oxidation, 1 gram of carbohydrate requires 7.3 grams of sulfuric acid; 1 gram of protein requires 9.0 grams; and 1 gram of fat requires 17.8 grams of sulfuric acid.[1]

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[1] Self, *Pharm. J.*, 88, 384 (1912).

Fifteen to eighteen grams of potassium or sodium sulfate are added to raise the boiling point of the sulfuric acid and thereby speed up the oxidation. There is approximately a 3° C. rise in boiling point of the sulfuric acid for each gram of potassium sulfate added.

An oxidation catalyst (0.7 gram mercuric oxide, 0.65 gram mercury, 0.3–0.5 gram crystalline copper sulfate, 0.25 gram selenium, or combination of two of these) is added to speed up the oxidation of the organic matter. The substances act as oxidation catalysts (oxygen carriers) because they readily pass from a higher to a lower valence and back again. Mercury and mercuric oxide were among the first to be used as oxidation catalysts and have proven to be very efficient. The following equations illustrate how mercury functions as an oxygen carrier in the reaction:

$$2\,\mathrm{HgSO_4} \xrightarrow[\text{reducing material}]{\text{in presence of}} \mathrm{Hg_2SO_4} + \mathrm{SO_3} + \mathrm{O}$$

$$\mathrm{Hg_2SO_4} + 2\,\mathrm{H_2SO_4} \rightarrow 2\,\mathrm{HgSO_4} + 2\,\mathrm{H_2O} + \mathrm{SO_2}.$$

If mercury is used as a catalyst, it must be precipitated with potassium sulfide before the distillation process since it forms a complex substance with ammonia which is not readily decomposed by alkali and therefore prevents the complete distillation of ammonia. Copper sulfate or metallic copper are effective catalysts and are frequently used. Selenium, suggested by Lauro,[1] has been used alone in the form of selenized granules (selenium deposited upon pumice stone) or in combination with either copper sulfate or mercuric oxide. There is some danger of losing nitrogen when selenium is used as a catalyst,[2, 3] the loss increasing with the amount of selenium used, but it is also reported[4] that no loss occurs if the selenium used does not exceed 0.25 gram.

Heat carefully over a low heat in a Kjeldahl digestion apparatus (Fig. 37) until the mixture no longer froths, then increase the heat so that the contents of the flask boil briskly. Digest the mixture until the solution loses its dark color and becomes clear, then continue the digestion for an additional 20–30 min. to insure complete oxidation. During digestion heat should not strike any portion of the flask that is not in contact with liquid or a decomposition of ammonium sulfate with subsequent loss of ammonia may occur.

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[1] Lauro, *Ind. Eng. Chem., Anal. Ed.*, **3**, 401 (1931).

[2] Davis and Wise, *Cer. Chem.*, **10**, 488 (1934).

[3] Sinder and Coleman, *Cer. Chem.*, **11**, 414 (1934).

[4] Bradstreet, *Ind. Eng. Chem., Anal. Ed.*, **12**, 657 (1940).

*Distillation Process.* Previous to the actual distillation, it is necessary to insure that the distillation apparatus is absolutely clean and free from ammonia. Shortly before its use, attach a Kjeldahl flask containing water to the condenser and distill 150–200 ml. of water through the apparatus, collecting the distillate and discarding it.

The ammonium sulfate—potassium sulfate—sulfuric acid mixture, either liquid or solid, resulting from the Kjeldahl digestion is dissolved in 300 ml. of water. This is necessary to reduce the violence of the reaction later when alkali is added. The digestion mixture *must be entirely dissolved in the water before the distillation process is attempted.*

Then measure 50.00 ml. of standard 0.1 N acid into a 500 ml. Erlenmeyer flask, add 3–5 drops of mixed methyl red indicator solution, and place under the condenser of the distilling unit, making sure that the condenser tube extends beneath the surface of the acid in the flask.

Pour 100 ml. of the Kjeldahl alkali solution into a graduated cylinder. Hold the Kjeldahl flask containing the diluted and cooled digest in an inclined position and pour the measured quantity of Kjeldahl alkali into the flask so that it runs down the neck of the flask and layers underneath the solution without mixing. (Loss of ammonia liberated by the action of alkali on ammonium sulfate is thus prevented by the upper acid layer in the flask.) Add a few pieces of granulated zinc to the flask and connect the flask to the condenser. Ignite the burner under the flask and quickly mix the contents of the flask thoroughly by shaking, using a rotary motion. It is advisable to start the distillation with a medium flame and, after the solution is boiling, increase the size of the flame until the solution boils briskly. After distilling 150–200 ml. of liquid, remove the receiving flask so that the tip of the condenser tube is above the liquid in the flask and wash off the condenser tube with distilled water. Then turn off the flame under the distilling flask and remove the receiving flask for titration.

Metallic zinc is added in the distillation to prevent bumping due to superheating of the solution and also furnishes nuclei for vapor bubble formation. Zinc, in an alkaline solution, slowly reacts to form a zincate and hydrogen. The slow evolution of hydrogen keeps the solution stirred, thereby preventing superheating.

$$Zn + 2\ NaOH \rightarrow Na_2ZnO_2 + H_2.$$

Usually a volume of 80–100 ml. of Kjeldahl alkali is sufficient to neutralize all the sulfuric acid in the Kjeldahl flask and produce an alkaline medium for the decomposition of the ammonium sulfate. If an extra quantity of the concentrated sulfuric acid was added during the digestion, more Kjeldahl alkali may be required. In this event, it is advisable to add 50 ml. to the flask, mix thoroughly, cool and then layer with the remainder of the alkali required and proceed according to the previous directions. An indicator, such as phenolphthalein, may be used in the flask to insure that the solution is alkaline after mixing.

The receiving flask normally contains a measured volume of standard acid sufficient to react with all the ammonia distilled and also to have an excess of acid remaining at the end of the distillation. An indicator (mixed methyl red, methyl red, or alizarin) is usually added to indicate the reaction in the flask. If the contents of the receiving flask become alkaline during the distillation, an added measured volume of the standard acid should be pipetted into the receiving flask.

To insure complete reaction of the ammonia distilled with the standard acid, the distilling tube should dip into the acid solution. The efficiency of this step may be further increased by using a distilling tube with its end blown into a small sphere having a number of perforations through which the distillate must pass. In this way, the gas and liquid distilled is broken up and passes into the standard acid in a finely divided condition, which is conducive to the complete absorption of the ammonia.

Just before the distillation is stopped, the flask containing the standard acid is moved so that the tip of the distilling tube is out of the liquid. Several milliliters of distillate are collected in this way insuring that the interior of the distillation tube has been washed free from standard acid. The outside of the distillation tube is then washed (by means of a wash bottle) and the washings collected in the receiving flask.

*Titration and Calculations.* Titrate the excess acid remaining in the receiving flask at the completion of the distillation process with standard 0.1 N alkali solution. The blank titration minus the sample titration represents the amount of acid neutralized by the ammonia from the sample, corrected for any ammonia derived from the reagents. Convert this value into grams of nitrogen and then into grams of protein (by an appropriate factor) and calculate the percentage of protein in the sample. A typical calculation is given below.

*Protein Factor.* The protein factor is derived from a knowledge of the percentage of nitrogen present in proteins. The average percentage of nitrogen in plant proteins is 16 per cent. The factor for converting nitrogen to protein would then be $\frac{100}{16}$ or 6.25. This general conversion factor (6.25) is used for all proteins except wheat flour (factor 5.7) and dairy products (factor 6.38), even though the exact nitrogen content of the proteins of a number of common agricultural products is known and an exact factor available.[1]

*Boric Acid Modification.*[2] A slight modification in the distillation and titration procedures is permissible which somewhat simplifies the method. Instead of placing 50.00 ml. of standard 0.1 N acid in the receiving flask, a 50 ml. volume of saturated boric acid solution, measured in a graduated cylinder, is added to the flask. It is not necessary to measure the volume accurately since the boric acid is not involved in the titration but simply reacts with and holds the ammonia as it is distilled into the flask. At the completion of the distillation, the distillate has a basic reaction to the ordinary indicators (mixed methyl red, methyl red, alizarin, etc.) and the ammonia is titrated directly with standard 0.1 N acid solution. This procedure eliminates the use of a standard alkali solution.

*Calculation.* Take, as an example, a 1.000 gram sample of material analyzed for its protein content. A 50.00 ml. volume of 0.0950 N acid was placed in the receiving flask for the sample and a like volume for the blank. At the completion of the distillation, 52.00 ml. of 0.0900 N alkali solution were used to titrate the excess acid in the blank, whereas 25.00 ml. of the standard alkali solution were required to titrate the excess acid in the sample.

Then:

52.00 − 25.00 = 27.00 ml. of 0.0900 N alkali solution equivalent to the ammonia distilled from the sample and corrected for any ammonia derived from the reagents.

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[1] Jones, Munsey and Walker, *J. Assoc. Off. Agr. Chem.*, 25, 118 (1942).

[2] Meeker and Wagner, *Ind. Eng. Chem., Anal. Ed.*, 5, 396 (1933).

27.00 × 0.0900 = 2.430 ml. of normal alkali solution, equivalent to the ammonia (or nitrogen) distilled from the sample.

0.014 × 2.43 = 0.0340 gram nitrogen present in the sample. (1 ml. of normal alkali solution is equivalent to 1 ml. of normal nitrogen solution, which contains 0.014 gram of nitrogen.)

0.0340 × 6.25 = 0.2125 gram protein present in the sample. (6.25 is the general protein factor for converting nitrogen to protein.)

0.2125 ÷ 1.000 × 100 = 21.25 per cent protein in the sample.

## ANALYSIS FOR FAT CONTENT

The various methods available will determine as fat all the fat-soluble materials present in the sample. These fat-soluble materials may include phospholipids, sterols, free fatty acids, carotinoid pigments, chlorophyll, etc., in addition to the fats. For this reason, the determination is frequently referred to as the crude fat or ether extract determination. Detailed procedures are given for the determination of fat in feeds (pp. 198–9), and in milk (pp. 208–13).

The several methods available for this determination may be grouped into two general classes: (1) dry extraction methods, and (2) wet extraction methods. As the names imply, dry extraction methods involve the removal of the fat soluble substances from thoroughly dried materials by means of an anhydrous solvent. Wet extractions separate, or remove, the fatty substances from the material without any drying of the sample analyzed.

**Dry Extraction Methods.** The material to be analyzed must be dried thoroughly in an oven and the solvent used for the extraction must be anhydrous. This is necessary to avoid the presence of any water so that water-soluble materials are not extracted and determined with the fat. Very frequently, the fat determination is made to follow a moisture determination and the dried sample used directly for the determination of fat.

The dried material may be subjected to *continuous* or *intermittent extraction* with a solvent. The two types of apparatus are illustrated in Fig. 39. In both types of apparatus, the weighed dry sample is placed in a cellulose or an alundum extraction thimble which, in turn, is placed into an extraction tube. The top of the extraction tube is attached to a water cooled condenser, preferably through ground glass joints. The bottom of the extraction tube is attached to a weighed flask either by a ground glass joint or a cork protected by tin foil. The extraction tube in the intermittent type of extraction apparatus is equipped with a siphon so that every 5 or 10 min. the solvent plus extracted fatty material siphons off and the sample is subjected to fresh solvent. In the continuous extraction apparatus, the solvent in the flask is continually being vaporized, liquefied in the condenser, drops upon and passes through the sample to fall back into the flask carrying with it any extracted matter.

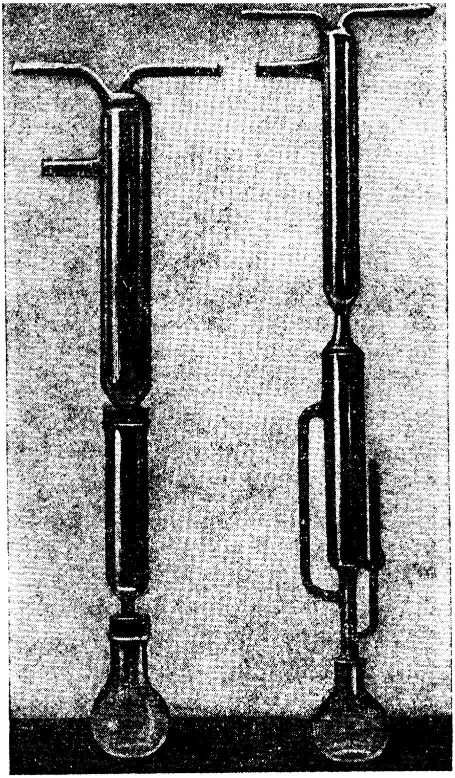

FIG. 39. Continuous and Intermittent Extractors.

Intermittent extraction setups, of which the Soxhlet type illustrated in Fig. 39 is the most common, are somewhat more efficient than continuous extraction setups. Furthermore, in the Soxhlet extractor, the solvent entirely surrounds and permeates the sample, thereby eliminating any channeling due to the solvent forming a channel and passing through only a portion of the sample, as may occur in the continuous extractors.

**Wet Extraction Methods.** Several types of wet extraction methods are available. One of the oldest of these methods is the Babcock method for determining the percentage of fat in milk and milk products (pp. 208–10).

In the *Babcock method*, the measured sample is placed in a special flask having a calibrated neck. The sample is treated with concentrated sulfuric acid which destroys the film surrounding the fat globules, permitting them to coalesce. After centrifuging to effect a more complete separation of the fat from the aqueous phase, water is added, forcing the fat column up into the calibrated neck of the flask so that the volume of the fat may be read, and from this the percentage of fat is calculated.

The *Röse-Gottlieb*[1] and *Mojonnier* methods exemplify another type of wet extraction methods. Both these methods have been used mainly in the analysis of milk and milk products (see pp. 210–13) although they may be adapted to other products.

In both the Röse-Gottlieb and Mojonnier methods, the measured sample is first treated with ethyl alcohol to precipitate the proteins in the layer surrounding the fat globules, then with ammonium hydroxide solution to cause the proteins to go into solution. As a result of this treatment, the fat is freed and coalesces in a layer. A 1:1 mixture of ethyl and petroleum ether is then added to dissolve the fat. The petroleum ether prevents the solution of any water-soluble materials by the ethyl ether. The ethers containing the dissolved fat are decanted or siphoned off into a weighed flask. The extraction is repeated a second time after which the solvents are evaporated and the weight of extracted fat determined.

## SUGAR ANALYSIS BY REDUCTION METHODS

By definition, the simple sugars are either aldehyde or ketone oxidation products of the polyhydroxy alcohols and so contain a free aldehyde or ketone group. The presence of either an aldehyde or ketone group adjacent to a hydroxy group confers reducing powers on the molecule which can then be oxidized easily. Thus all monosaccharides may be oxidized and all are classified as reducing sugars.

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[1] Röse, *Z. angew. Chem.*, p. 100 (1888). Assoc. Off. Agr. Chem., "Methods of Analysis," 5th Ed. (1940), p. 272.

Disaccharides may or may not be reducing sugars. If, in the condensation of two monosaccharides, the aldehyde or ketone group of each monosaccharide is used up in connecting the two monosaccharides there is no longer a free aldehyde or ketone group present in the molecule and, therefore, the disaccharide does not show reducing properties. It is for this reason that sucrose is a non-reducing sugar. If, on the other hand, the aldehyde or ketone group of one monosaccharide is connected to an alcohol group of another in forming a disaccharide, there is a free aldehyde or ketone group left in the molecule and such a disaccharide possesses reducing powers.

Most of the reduction methods involve the reduction of copper in an alkaline or acid medium. The determination of the reduced copper may be accomplished by gravimetric, volumetric, colorimetric, or electrolytic methods.

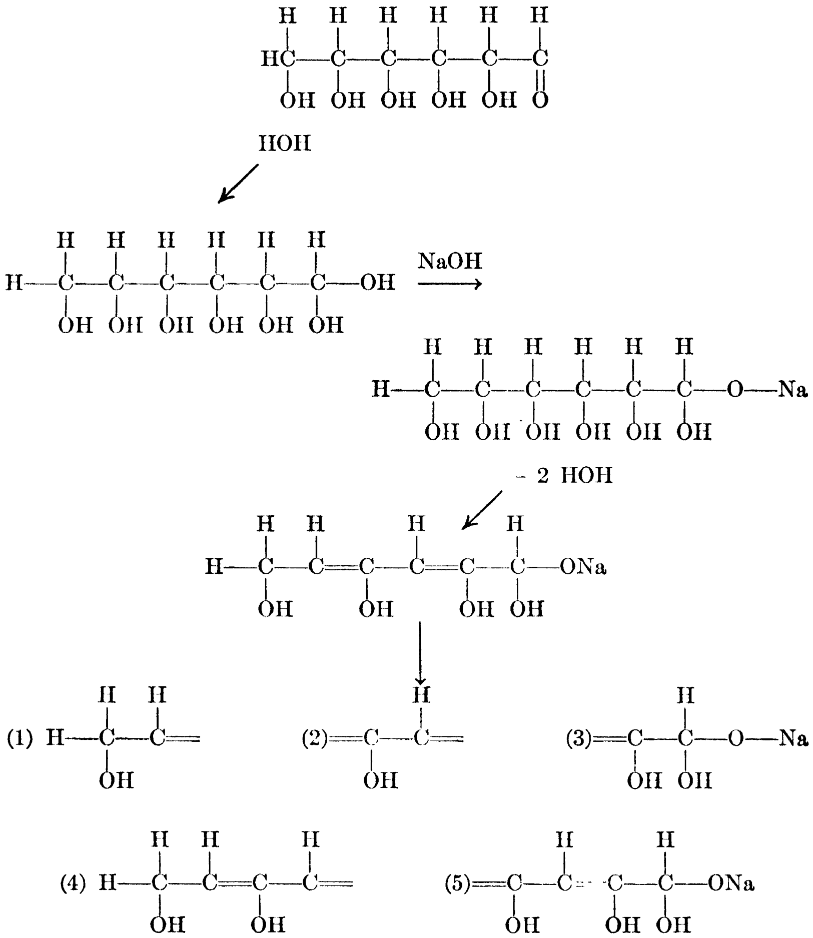
Solutions in which sugar is to be determined by reduction methods must be clarified to remove organic matter which would precipitate with the reduced copper. Furthermore, the presence of proteins (protective colloids) would prevent the formation of proper sized cuprous oxide crystals, thereby preventing the quantitative separation of such crystals from the solution by filtration.

**Munson and Walker Method.** One of the older and most common of the copper reduction methods is that of Munson and Walker. In this method, the sugar solution is heated with Fehling's solution under strictly empirical conditions. The amount of copper reduced is determined and the corresponding amount of sugar read from a table.

Fehling's solution is, in reality, a mixture of equal proportions of two solutions: (*a*) a copper sulfate solution, and (*b*) an alkaline tartrate solution. These two solutions are not mixed previous to the determination since the mixture is not stable for any great length of time.

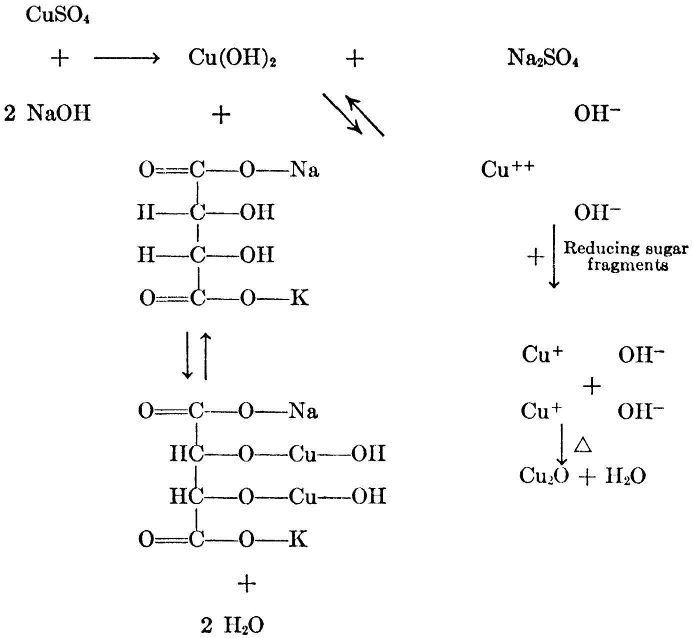
Fehling's solution performs a two-fold purpose. It furnishes a solution containing copper ions which are reduced by the sugar to cuprous ions and, in addition, the alkalinity is such that the sugar molecules are broken up into reactive fragments. The two series of reactions which take place when Fehling's solution is heated in the presence of a reducing sugar solution are illustrated diagrammatically as follows:

I. The action of sodium hydroxide in Fehling's solution and heat on a reducing sugar (for example glucose) to form certain possible reactive fragments:



The glucose, as is characteristic of aldehyde compounds, easily opens up its double bonds between carbon and oxygen and adds water to form a polyhydric alcohol. One of the hydrogens of glucose (very likely the hydrogen of the hydrated aldol group) behaves as an acid hydrogen and so is slightly ionized. Upon treatment with sodium hydroxide, this hydrogen is replaced by sodium. The salt is unstable and the molecule first forms enols and then breaks into a number of fragments. It is believed that 3–4 reactive fragments are produced when glucose is heated with Fehling's solution. These fragments are readily oxidized and cause the reduction of cupric ions to the cuprous state.

II. The reaction of sodium hydroxide, copper sulfate, and Rochelle salt when heated in the presence of reducing sugar fragments:



The copper sulfate reacts with sodium hydroxide to form cupric hydroxide and sodium sulfate. Most of the cupric hydroxide (normally insoluble) reacts with the Rochelle salt to form a complex compound, which is soluble and holds the copper in solution. However, this is an equilibrium reaction and, as fast as the copper hydroxide which is in solution is removed, copper will leave the complex to restore the equilibrium. The small amount of copper hydroxide which is in solution is ionized to a considerable extent and exists in equilibrium with cupric and hydroxide ions. As the cupric ions are reduced by the sugar fragments, more of the soluble copper hydroxide ionizes to give cupric ions to restore the equilibrium. In this way, the entire amount of copper present may be reduced. The reduced cuprous hydroxide loses water in the presence of heat to give insoluble cuprous oxide.

The Munson and Walker method itself, irrespective of the way in which the reduced copper is determined, is strictly empirical. The concentration of reagents employed affects the amount of copper reduced so care must be exercised to prepare solutions of the correct concentration. The length of time the solution is heated during the reduction process and the time required to bring the solution to boil must be as close to the stipulated time as possible, since increased heating causes an increase in the amount of copper reduced. It is especially important that the solution boil *exactly* 2 min. and be filtered immediately and quickly, since the reduction of the copper will continue in the hot solution until it is filtered. The size of beaker is important as the amount of copper reduced is directly proportional to the lateral area of the glass exposed to the solution and inversely proportional to the top and bottom.

While sucrose is considered a non-reducing sugar, it does cause some reduction of copper under the conditions of the method. Increasing concentrations of sucrose increase the amount of copper reduced. To correct for this, the Munson and Walker table (Table 12) has separate columns for invert sugar determined in the presence of two different concentrations of sucrose and also for lactose in the presence of sucrose.

It is advisable in the determination to use a quantity of sample such that the values will fall near the center of the table. Values at either end of the table are open to somewhat greater error. This is especially true for the beginning values in the table dealing with the lower sugar concentrations.

*Reagents.*

1. *Fehling's Copper Sulfate Solution.* Dissolve 34.639 grams of copper sulfate crystals ($CuSO_4 \cdot 5\,H_2O$) in water and dilute to a volume of 500 ml. Filter through prepared asbestos and store in a clean dry bottle.
2. *Fehling's Alkaline Tartrate Solution.* Dissolve 173 grams of Rochelle salts (sodium potassium tartrate) and 50 grams of sodium hydroxide in water and dilute to a volume of 500 ml. Let stand for two days, filter through prepared asbestos, and store in a clean dry bottle with a rubber stopper.
3. *Asbestos.* The asbestos used should be acid and alkali digested. This is accomplished by first letting the asbestos stand in a solution of 1 part hydrochloric acid to 3 parts of water for 2–3 days. Wash the asbestos free from acid and place in a 10 per cent sodium hydroxide solution for 2–3 days. Treat for a few hours with hot alkaline tartrate solution prepared as above. Wash the asbestos free from alkali and let stand for several hours in a solution of 1 part nitric acid to 3 parts of water. Wash the asbestos free from acid and suspend in distilled water.

## TABLE 12.* MUNSON AND WALKER'S TABLE FOR CALCULATING DEXTROSE, INVERT SUGAR ALONE, INVERT SUGAR IN THE PRESENCE OF SUCROSE (0.4 GRAM AND 2 GRAMS TOTAL SUGAR), LACTOSE, LACTOSE AND SUCROSE (2 MIXTURES), AND MALTOSE (CRYSTALLIZED)† (Expressed in Milligrams)

| Cuprous Oxide ($Cu_2O$) | Copper (Cu) | Dextrose (*d*-Glucose) | Invert Sugar | Invert Sugar and Sucrose | | Lactose | Lactose and Sucrose | | Maltose | Cuprous Oxide ($Cu_2O$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 0.4 Gram Total Sugar | 2 Grams Total Sugar | $C_{12}H_{22}O_{11}+H_2O$ | 1 Lactose, 4 Sucrose | 1 Lactose, 12 Sucrose | $C_{12}H_{22}O_{11}+H_2O$ | |
| 10 | 8.9 | 4.0 | 4.5 | 1.6 | ..... | 6.3 | 6.1 | ..... | 6.2 | 10 |
| 12 | 10.7 | 4.9 | 5.4 | 2.5 | ...... | 7.5 | 7.3 | ...... | 7.9 | 12 |
| 14 | 12.4 | 5.7 | 6.3 | 3.4 | ...... | 8.8 | 8.5 | ...... | 9.5 | 14 |
| 16 | 14.2 | 6.6 | 7.2 | 4.3 | ...... | 10.0 | 9.7 | ...... | 11.2 | 16 |
| 18 | 16.0 | 7.5 | 8.1 | 5.2 | ...... | 11.3 | 10.9 | ...... | 12.9 | 18 |
| 20 | 17.8 | 8.3 | 8.9 | 6.1 | ...... | 12.5 | 12.1 | ...... | 14.6 | 20 |
| 22 | 19.5 | 9.2 | 9.8 | 7.0 | ...... | 13.8 | 13.3 | ...... | 16.2 | 22 |
| 24 | 21.3 | 10.0 | 10.7 | 7.9 | ...... | 15.0 | 14.5 | ...... | 17.9 | 24 |
| 26 | 23.1 | 10.9 | 11.6 | 8.8 | ...... | 16.3 | 15.8 | ...... | 19.6 | 26 |
| 28 | 24.9 | 11.8 | 12.5 | 9.7 | ...... | 17.6 | 17.0 | ...... | 21.2 | 28 |
| 30 | 26.6 | 12.6 | 13.4 | 10.7 | 4.3 | 18.8 | 18.2 | ...... | 22.9 | 30 |
| 32 | 28.4 | 13.5 | 14.3 | 11.6 | 5.2 | 20.1 | 19.4 | ...... | 24.6 | 32 |
| 34 | 30.2 | 14.3 | 15.2 | 12.5 | 6.1 | 21.4 | 20.7 | ...... | 26.2 | 34 |
| 36 | 32.0 | 15.2 | 16.1 | 13.4 | 7.0 | 22.8 | 22.0 | ...... | 27.9 | 36 |
| 38 | 33.8 | 16.1 | 16.9 | 14.3 | 7.9 | 24.2 | 23.3 | ...... | 29.6 | 38 |
| 40 | 35.5 | 16.9 | 17.8 | 15.2 | 8.8 | 25.5 | 24.7 | ...... | 31.3 | 40 |
| 42 | 37.3 | 17.8 | 18.7 | 16.1 | 9.7 | 26.9 | 26.0 | ...... | 32.9 | 42 |
| 44 | 39.1 | 18.7 | 19.6 | 17.0 | 10.7 | 28.3 | 27.3 | ...... | 34.6 | 44 |
| 46 | 40.9 | 19.6 | 20.5 | 17.9 | 11.6 | 29.6 | 28.6 | ...... | 36.3 | 46 |
| 48 | 42.6 | 20.4 | 21.4 | 18.8 | 12.5 | 31.0 | 30.0 | ...... | 37.9 | 48 |
| 50 | 44.4 | 21.3 | 22.3 | 19.7 | 13.4 | 32.3 | 31.3 | ...... | 39.6 | 50 |
| 52 | 46.2 | 22.2 | 23.2 | 20.7 | 14.3 | 33.7 | 32.6 | ...... | 41.3 | 52 |
| 54 | 48.0 | 23.0 | 24.1 | 21.6 | 15.2 | 35.1 | 34.0 | ...... | 42.9 | 54 |
| 56 | 49.7 | 23.9 | 25.0 | 22.5 | 16.2 | 36.4 | 35.3 | ...... | 44.6 | 56 |
| 58 | 51.5 | 24.8 | 25.9 | 23.4 | 17.1 | 37.8 | 36.6 | ...... | 46.3 | 58 |
| 60 | 53.3 | 25.6 | 26.8 | 24.3 | 18.0 | 39.2 | 37.9 | ...... | 48.0 | 60 |
| 62 | 55.1 | 26.5 | 27.7 | 25.2 | 18.9 | 40.5 | 39.3 | ...... | 49.6 | 62 |
| 64 | 56.8 | 27.4 | 28.6 | 26.2 | 19.8 | 41.9 | 40.6 | ...... | 51.3 | 64 |
| 66 | 58.6 | 28.3 | 29.5 | 27.1 | 20.8 | 43.3 | 41.9 | ...... | 53.0 | 66 |
| 68 | 60.4 | 29.2 | 30.4 | 28.0 | 21.7 | 44.7 | 43.3 | 40.7 | 54.6 | 68 |
| 70 | 62.2 | 30.0 | 31.3 | 28.9 | 22.6 | 46.0 | 44.6 | 41.9 | 56.3 | 70 |
| 72 | 64.0 | 30.9 | 32.3 | 29.8 | 23.5 | 47.4 | 45.9 | 43.1 | 58.0 | 72 |
| 74 | 65.7 | 31.8 | 33.2 | 30.8 | 24.5 | 48.8 | 47.3 | 44.2 | 59.6 | 74 |
| 76 | 67.5 | 32.7 | 34.1 | 31.7 | 25.4 | 50.1 | 48.6 | 45.4 | 61.3 | 76 |
| 78 | 69.3 | 33.6 | 35.0 | 32.6 | 26.3 | 51.5 | 49.9 | 46.6 | 63.0 | 78 |
| 80 | 71.1 | 34.4 | 35.9 | 33.5 | 27.3 | 52.9 | 51.3 | 47.8 | 64.6 | 80 |
| 82 | 72.8 | 35.3 | 36.8 | 34.5 | 28.2 | 54.2 | 52.6 | 49.0 | 66.3 | 82 |
| 84 | 74.6 | 36.2 | 37.7 | 35.4 | 29.1 | 55.6 | 53.9 | 50.1 | 68.0 | 84 |
| 86 | 76.4 | 37.1 | 38.6 | 36.3 | 30.0 | 57.0 | 55.3 | 51.3 | 69.7 | 86 |
| 88 | 78.2 | 38.0 | 39.5 | 37.2 | 31.0 | 58.4 | 56.6 | 52.5 | 71.3 | 88 |

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* From the Assoc. Off. Agr. Chem., "Methods of Analysis" (1940). Levulose Equivalents are given in Hammond's Table (Table 14, pp. 174–5).

† U. S. Bur. Standards Circ. 44, p. 321. The columns headed "Lactose" and "Lactose and Sucrose" are taken from "Methods of Sugar Analysis and Allied Determinations" by Arthur Given.

TABLE 12. MUNSON AND WALKER'S TABLE.—*Continued*

(Expressed in Milligrams)

| Cuprous Oxide ($Cu_2O$) | Copper (Cu) | Dextrose (*d*-Glucose) | Invert Sugar | Invert Sugar and Sucrose | | Lactose | Lactose and Sucrose | | Maltose | Cuprous Oxide ($Cu_2O$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 0.4 Gram Total Sugar | 2 Grams Total Sugar | $C_{12}H_{22}O_{11}+H_2O$ | 1 Lactose, 4 Sucrose | 1 Lactose, 12 Sucrose | $C_{12}H_{22}O_{11}+H_2O$ | |
| 90 | 79.9 | 38.9 | 40.4 | 38.2 | 31.9 | 59.7 | 57.9 | 53.7 | 73.0 | 90 |
| 92 | 81.7 | 39.8 | 41.4 | 39.1 | 32.8 | 61.1 | 59.3 | 54.9 | 74.7 | 92 |
| 94 | 83.5 | 40.6 | 42.3 | 40.0 | 33.8 | 62.5 | 60.6 | 56.0 | 76.3 | 94 |
| 96 | 85.3 | 41.5 | 43.2 | 41.0 | 34.7 | 63.8 | 61.9 | 57.2 | 78.0 | 96 |
| 98 | 87.1 | 42.4 | 44.1 | 41.9 | 35.6 | 65.2 | 63.3 | 58.4 | 79.7 | 98 |
| 100 | 88.8 | 43.3 | 45.0 | 42.8 | 36.6 | 66.6 | 64.6 | 59.6 | 81.3 | 100 |
| 102 | 90.6 | 44.2 | 46.0 | 43.8 | 37.5 | 68.0 | 66.0 | 60.8 | 83.0 | 102 |
| 104 | 92.4 | 45.1 | 46.9 | 44.7 | 38.5 | 69.3 | 67.3 | 62.0 | 84.7 | 104 |
| 106 | 94.2 | 46.0 | 47.8 | 45.6 | 39.4 | 70.7 | 68.6 | 63.2 | 86.3 | 106 |
| 108 | 95.9 | 46.9 | 48.7 | 46.6 | 40.3 | 72.1 | 70.0 | 64.4 | 88.0 | 108 |
| 110 | 97.7 | 47.8 | 49.6 | 47.5 | 41.3 | 73.5 | 71.3 | 65.6 | 89.7 | 110 |
| 112 | 99.5 | 48.7 | 50.6 | 48.4 | 42.2 | 74.8 | 72.6 | 66.7 | 91.3 | 112 |
| 114 | 101.3 | 49.6 | 51.5 | 49.4 | 43.2 | 76.2 | 74.0 | 67.9 | 93.0 | 114 |
| 116 | 103.0 | 50.5 | 52.4 | 50.3 | 44.1 | 77.6 | 75.3 | 69.1 | 94.7 | 116 |
| 118 | 104.8 | 51.4 | 53.3 | 51.2 | 45.0 | 79.0 | 76.7 | 70.3 | 96.4 | 118 |
| 120 | 106.6 | 52.3 | 54.3 | 52.2 | 46.0 | 80.3 | 78.0 | 71.5 | 98.0 | 120 |
| 122 | 108.4 | 53.2 | 55.2 | 53.1 | 46.9 | 81.7 | 79.3 | 72.7 | 99.7 | 122 |
| 124 | 110.1 | 54.1 | 56.1 | 54.1 | 47.9 | 83.1 | 80.7 | 73.9 | 101.4 | 124 |
| 126 | 111.9 | 55.0 | 57.0 | 55.0 | 48.8 | 84.5 | 82.0 | 75.1 | 103.0 | 126 |
| 128 | 113.7 | 55.9 | 58.0 | 55.9 | 49.8 | 85.8 | 83.4 | 76.3 | 104.7 | 128 |
| 130 | 115.5 | 56.8 | 58.9 | 56.9 | 50.7 | 87.2 | 84.7 | 77.5 | 106.4 | 130 |
| 132 | 117.3 | 57.7 | 59.8 | 57.8 | 51.7 | 88.6 | 86.0 | 78.7 | 108.0 | 132 |
| 134 | 119.0 | 58.6 | 60.8 | 58.8 | 52.6 | 90.0 | 87.4 | 79.7 | 109.7 | 134 |
| 136 | 120.8 | 59.5 | 61.7 | 59.7 | 53.6 | 91.3 | 88.7 | 81.1 | 111.4 | 136 |
| 138 | 122.6 | 60.4 | 62.6 | 60.7 | 54.5 | 92.7 | 90.1 | 82.3 | 113.0 | 138 |
| 140 | 124.4 | 61.3 | 63.6 | 61.6 | 55.5 | 94.1 | 91.4 | 83.5 | 114.7 | 140 |
| 142 | 126.1 | 62.2 | 64.5 | 62.6 | 56.4 | 95.5 | 92.8 | 84.7 | 116.4 | 142 |
| 144 | 127.9 | 63.1 | 65.4 | 63.5 | 57.4 | 96.8 | 94.1 | 85.9 | 118.0 | 144 |
| 146 | 129.7 | 64.0 | 66.4 | 64.5 | 58.3 | 98.2 | 95.4 | 87.1 | 119.7 | 146 |
| 148 | 131.5 | 65.0 | 67.3 | 65.4 | 59.3 | 99.6 | 96.8 | 88.3 | 121.4 | 148 |
| 150 | 133.2 | 65.9 | 68.3 | 66.4 | 60.2 | 101.0 | 98.1 | 89.5 | 123.0 | 150 |
| 152 | 135.0 | 66.8 | 69.2 | 67.3 | 61.2 | 102.3 | 99.5 | 90.8 | 124.7 | 152 |
| 154 | 136.8 | 67.7 | 70.1 | 68.3 | 62.1 | 103.7 | 100.8 | 92.0 | 126.4 | 154 |
| 156 | 138.6 | 68.6 | 71.1 | 69.2 | 63.1 | 105.1 | 102.2 | 93.2 | 128.0 | 156 |
| 158 | 140.3 | 69.5 | 72.0 | 70.2 | 64.1 | 106.5 | 103.5 | 94.4 | 129.7 | 158 |
| 160 | 142.1 | 70.4 | 73.0 | 71.2 | 65.0 | 107.9 | 104.8 | 95.6 | 131.4 | 160 |
| 162 | 143.9 | 71.4 | 73.9 | 72.1 | 66.0 | 109.2 | 106.2 | 96.8 | 133.0 | 162 |
| 164 | 145.7 | 72.3 | 74.9 | 73.1 | 66.9 | 110.6 | 107.5 | 98.0 | 134.7 | 164 |
| 166 | 147.5 | 73.2 | 75.8 | 74.0 | 67.9 | 112.0 | 108.9 | 99.2 | 136.4 | 166 |
| 168 | 149.2 | 74.1 | 76.8 | 75.0 | 68.9 | 113.4 | 110.2 | 100.4 | 138.0 | 168 |

TABLE 12. MUNSON AND WALKER'S TABLE.—*Continued*
(Expressed in Milligrams)

| Cuprous Oxide ($Cu_2O$) | Copper (Cu) | Dextrose (*d*-Glucose) | Invert Sugar | Invert Sugar and Sucrose | | Lactose | Lactose and Sucrose | | Maltose | Cuprous Oxide ($Cu_2O$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 0.4 Gram Total Sugar | 2 Grams Total Sugar | $C_{12}H_{22}O_{11}+H_2O$ | 1 Lactose, 4 Sucrose | 1 Lactose, 12 Sucrose | $C_{12}H_{22}O_{11}+H_2O$ | |
| 170 | 151.0 | 75.1 | 77.7 | 76.0 | 69.8 | 114.8 | 111.6 | 101.6 | 139.7 | 170 |
| 172 | 152.8 | 76.0 | 78.7 | 76.9 | 70.8 | 116.1 | 112.9 | 102.8 | 141.4 | 172 |
| 174 | 154.6 | 76.9 | 79.6 | 77.9 | 71.7 | 117.5 | 114.3 | 104.1 | 143.0 | 174 |
| 176 | 156.3 | 77.8 | 80.6 | 78.8 | 72.7 | 118.9 | 115.6 | 105.3 | 144.7 | 176 |
| 178 | 158.1 | 78.8 | 81.5 | 79.8 | 73.7 | 120.3 | 117.0 | 106.5 | 146.4 | 178 |
| 180 | 159.9 | 79.7 | 82.5 | 80.8 | 74.6 | 121.6 | 118.3 | 107.7 | 148.0 | 180 |
| 182 | 161.7 | 80.6 | 83.4 | 81.7 | 75.6 | 123.1 | 119.7 | 108.9 | 149.7 | 182 |
| 184 | 163.4 | 81.5 | 84.4 | 82.7 | 76.6 | 124.3 | 121.0 | 110.1 | 151.4 | 184 |
| 186 | 165.2 | 82.5 | 85.3 | 83.7 | 77.6 | 125.8 | 122.4 | 111.3 | 153.0 | 186 |
| 188 | 167.0 | 83.4 | 86.3 | 84.6 | 78.5 | 127.2 | 123.7 | 112.5 | 154.7 | 188 |
| 190 | 168.8 | 84.3 | 87.2 | 85.6 | 79.5 | 128.5 | 125.1 | 113.8 | 156.4 | 190 |
| 192 | 170.5 | 85.3 | 88.2 | 86.6 | 80.5 | 129.9 | 126.4 | 115.0 | 158.0 | 192 |
| 194 | 172.3 | 86.2 | 89.2 | 87.6 | 81.4 | 131.3 | 127.8 | 116.2 | 159.7 | 194 |
| 196 | 174.1 | 87.1 | 90.1 | 88.5 | 82.4 | 132.7 | 129.2 | 117.4 | 161.4 | 196 |
| 198 | 175.9 | 88.1 | 91.1 | 89.5 | 83.4 | 134.1 | 130.5 | 118.6 | 163.0 | 198 |
| 200 | 177.7 | 89.0 | 92.0 | 90.5 | 84.4 | 135.4 | 131.9 | 119.8 | 164.7 | 200 |
| 202 | 179.4 | 89.9 | 93.0 | 91.4 | 85.3 | 136.8 | 133.2 | 121.0 | 166.4 | 202 |
| 204 | 181.2 | 90.9 | 94.0 | 92.4 | 86.3 | 138.2 | 134.6 | 122.3 | 168.0 | 204 |
| 206 | 183.0 | 91.8 | 94.9 | 93.4 | 87.3 | 139.6 | 135.9 | 123.5 | 169.7 | 206 |
| 208 | 184.8 | 92.8 | 95.9 | 94.4 | 88.3 | 141.0 | 137.3 | 124.7 | 171.4 | 208 |
| 210 | 186.5 | 93.7 | 96.9 | 95.4 | 89.2 | 142.3 | 138.6 | 126.0 | 173.0 | 210 |
| 212 | 188.3 | 94.6 | 97.8 | 96.3 | 90.2 | 143.7 | 140.0 | 127.2 | 174.7 | 212 |
| 214 | 190.1 | 95.6 | 98.8 | 97.3 | 91.2 | 145.1 | 141.4 | 128.4 | 176.4 | 214 |
| 216 | 191.9 | 96.5 | 99.8 | 98.3 | 92.2 | 146.5 | 142.7 | 129.6 | 178.0 | 216 |
| 218 | 193.6 | 97.5 | 100.8 | 99.3 | 93.2 | 147.9 | 144.1 | 130.9 | 179.7 | 218 |
| 220 | 195.4 | 98.4 | 101.7 | 100.3 | 94.2 | 149.3 | 145.4 | 132.1 | 181.4 | 220 |
| 222 | 197.2 | 99.4 | 102.7 | 101.2 | 95.1 | 150.7 | 146.8 | 133.3 | 183.0 | 222 |
| 224 | 199.0 | 100.3 | 103.7 | 102.2 | 96.1 | 152.0 | 148.1 | 134.5 | 184.7 | 224 |
| 226 | 200.7 | 101.3 | 104.6 | 103.2 | 97.1 | 153.4 | 149.5 | 135.8 | 186.4 | 226 |
| 228 | 202.5 | 102.2 | 105.6 | 104.2 | 98.1 | 154.8 | 150.8 | 137.0 | 188.0 | 228 |
| 230 | 204.3 | 103.2 | 106.6 | 105.2 | 99.1 | 156.2 | 152.2 | 138.2 | 189.7 | 230 |
| 232 | 206.1 | 104.1 | 107.6 | 106.2 | 100.1 | 157.6 | 153.6 | 139.4 | 191.3 | 232 |
| 234 | 207.9 | 105.1 | 108.6 | 107.2 | 101.1 | 159.0 | 154.9 | 140.7 | 193.0 | 234 |
| 236 | 209.6 | 106.0 | 109.5 | 108.2 | 102.1 | 160.3 | 156.3 | 141.9 | 194.7 | 236 |
| 238 | 211.4 | 107.0 | 110.5 | 109.2 | 103.1 | 161.7 | 157.6 | 143.2 | 196.3 | 238 |
| 240 | 213.2 | 108.0 | 111.5 | 110.1 | 104.0 | 163.1 | 159.0 | 144.4 | 198.0 | 240 |
| 242 | 215.0 | 108.9 | 112.5 | 111.1 | 105.0 | 164.5 | 160.3 | 145.6 | 199.7 | 242 |
| 244 | 216.7 | 109.9 | 113.5 | 112.1 | 106.0 | 165.9 | 161.7 | 146.9 | 201.3 | 244 |
| 246 | 218.5 | 110.8 | 114.5 | 113.1 | 107.0 | 167.3 | 163.1 | 148.1 | 203.0 | 246 |
| 248 | 220.3 | 111.8 | 115.4 | 114.1 | 108.0 | 168.7 | 164.4 | 149.3 | 204.7 | 248 |

TABLE 12. MUNSON AND WALKER'S TABLE.—*Continued*

(Expressed in Milligrams)

| Cuprous Oxide ($Cu_2O$) | Copper (Cu) | Dextrose (*d*-Glucose) | Invert Sugar | Invert Sugar and Sucrose | | Lactose | Lactose and Sucrose | | Maltose | Cuprous Oxide ($Cu_2O$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 0.4 Gram Total Sugar | 2 Grams Total Sugar | $C_{12}H_{22}O_{11}+H_2O$ | 1 Lactose, 4 Sucrose | 1 Lactose, 12 Sucrose | $C_{12}H_{22}O_{11}+H_2O$ | |
| 250 | 222.1 | 112.8 | 116.4 | 115.1 | 109.0 | 170.1 | 165.8 | 150.6 | 206.3 | 250 |
| 252 | 223.8 | 113.7 | 117.4 | 116.1 | 110.0 | 171.5 | 167.2 | 151.8 | 208.0 | 252 |
| 254 | 225.6 | 114.7 | 118.4 | 117.1 | 111.0 | 172.8 | 168.5 | 153.1 | 209.7 | 254 |
| 256 | 227.4 | 115.7 | 119.4 | 118.1 | 112.0 | 174.2 | 169.9 | 154.3 | 211.3 | 256 |
| 258 | 229.2 | 116.6 | 120.4 | 119.1 | 113.0 | 175.6 | 171.3 | 155.5 | 213.0 | 258 |
| 260 | 231.0 | 117.6 | 121.4 | 120.1 | 114.0 | 177.0 | 172.6 | 156.8 | 214.7 | 260 |
| 262 | 232.7 | 118.6 | 122.4 | 121.1 | 115.0 | 178.4 | 174.0 | 158.0 | 216.3 | 262 |
| 264 | 234.5 | 119.5 | 123.4 | 122.1 | 116.0 | 179.8 | 175.3 | 159.3 | 218.0 | 264 |
| 266 | 236.3 | 120.5 | 124.4 | 123.1 | 117.0 | 181.2 | 176.7 | 160.5 | 219.7 | 266 |
| 268 | 238.1 | 121.5 | 125.4 | 124.1 | 118.0 | 182.6 | 178.1 | 161.8 | 221.3 | 268 |
| 270 | 239.8 | 122.5 | 126.4 | 125.1 | 119.0 | 184.0 | 179.4 | 163.0 | 223.0 | 270 |
| 272 | 241.6 | 123.4 | 127.4 | 126.2 | 120.0 | 185.3 | 180.8 | 164.3 | 224.6 | 272 |
| 274 | 243.4 | 124.4 | 128.4 | 127.2 | 121.1 | 186.7 | 182.2 | 165.5 | 226.3 | 274 |
| 276 | 245.2 | 125.4 | 129.4 | 128.2 | 122.1 | 188.1 | 183.5 | 166.8 | 228.0 | 276 |
| 278 | 246.9 | 126.4 | 130.4 | 129.2 | 123.1 | 189.5 | 184.9 | 168.0 | 229.6 | 278 |
| 280 | 248.7 | 127.3 | 131.4 | 130.2 | 124.1 | 190.9 | 186.3 | 169.3 | 231.3 | 280 |
| 282 | 250.5 | 128.3 | 132.4 | 131.2 | 125.1 | 192.3 | 187.6 | 170.5 | 233.0 | 282 |
| 284 | 252.3 | 129.3 | 133.4 | 132.2 | 126.1 | 193.7 | 189.0 | 171.8 | 234.6 | 284 |
| 286 | 254.0 | 130.3 | 134.4 | 133.2 | 127.1 | 195.1 | 190.4 | 173.0 | 236.3 | 286 |
| 288 | 255.8 | 131.3 | 135.4 | 134.3 | 128.1 | 196.5 | 191.7 | 174.3 | 238.0 | 288 |
| 290 | 257.6 | 132.3 | 136.4 | 135.3 | 129.2 | 197.8 | 193.1 | 175.5 | 239.6 | 290 |
| 292 | 259.4 | 133.2 | 137.4 | 136.3 | 130.2 | 199.2 | 194.4 | 176.8 | 241.3 | 292 |
| 294 | 261.2 | 134.2 | 138.4 | 137.3 | 131.2 | 200.6 | 195.8 | 178.1 | 242.9 | 294 |
| 296 | 262.9 | 135.2 | 139.4 | 138.3 | 132.2 | 202.0 | 197.2 | 179.3 | 244.6 | 296 |
| 298 | 264.7 | 136.2 | 140.5 | 139.4 | 133.2 | 203.4 | 198.6 | 180.6 | 246.3 | 298 |
| 300 | 266.5 | 137.2 | 141.5 | 140.4 | 134.2 | 204.8 | 199.9 | 181.8 | 247.9 | 300 |
| 302 | 268.3 | 138.2 | 142.5 | 141.4 | 135.3 | 206.2 | 201.3 | 183.1 | 249.6 | 302 |
| 304 | 270.0 | 139.2 | 143.5 | 142.4 | 136.3 | 207.6 | 202.7 | 184.4 | 251.3 | 304 |
| 306 | 271.8 | 140.2 | 144.5 | 143.4 | 137.3 | 209.0 | 204.0 | 185.6 | 252.9 | 306 |
| 308 | 273.6 | 141.2 | 145.5 | 144.5 | 138.3 | 210.4 | 205.4 | 186.9 | 254.6 | 308 |
| 310 | 275.4 | 142.2 | 146.6 | 145.5 | 139.4 | 211.8 | 206.8 | 188.1 | 256.3 | 310 |
| 312 | 277.1 | 143.2 | 147.6 | 146.5 | 140.4 | 213.2 | 208.1 | 189.4 | 257.9 | 312 |
| 314 | 278.9 | 144.2 | 148.6 | 147.6 | 141.4 | 214.6 | 209.5 | 190.7 | 259.6 | 314 |
| 316 | 280.7 | 145.2 | 149.6 | 148.6 | 142.4 | 216.0 | 210.9 | 191.9 | 261.2 | 316 |
| 318 | 282.5 | 146.2 | 150.7 | 149.6 | 143.5 | 217.3 | 212.2 | 193.2 | 262.9 | 318 |
| 320 | 284.2 | 147.2 | 151.7 | 150.7 | 144.5 | 218.7 | 213.6 | 194.4 | 264.6 | 320 |
| 322 | 286.0 | 148.2 | 152.7 | 151.7 | 145.5 | 220.1 | 215.5 | 195.7 | 266.2 | 322 |
| 324 | 287.8 | 149.2 | 153.7 | 152.7 | 146.6 | 221.5 | 216.4 | 197.0 | 267.9 | 324 |
| 326 | 289.6 | 150.2 | 154.8 | 153.8 | 147.6 | 222.9 | 217.7 | 198.2 | 269.6 | 326 |
| 328 | 291.4 | 151.2 | 155.8 | 154.8 | 148.6 | 224.3 | 219.1 | 199.5 | 271.2 | 328 |

TABLE 12. MUNSON AND WALKER'S TABLE.—*Continued*
(Expressed in Milligrams)

| Cuprous Oxide ($Cu_2O$) | Copper (Cu) | Dextrose (*d*-Glucose) | Invert Sugar | Invert Sugar and Sucrose | | Lactose | Lactose and Sucrose | | Maltose | Cuprous Oxide ($Cu_2O$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 0.4 Gram Total Sugar | 2 Grams Total Sugar | $C_{12}H_{22}O_{11}+H_2O$ | 1 Lactase, 4 Sucrose | 1 Lactose, 12 Sucrose | $C_{12}H_{22}O_{11}+H_2O$ | |
| 330 | 293.1 | 152.2 | 156.8 | 155.8 | 149.7 | 225.7 | 220.5 | 200.8 | 272.9 | 330 |
| 332 | 294.9 | 153.2 | 157.9 | 156.9 | 150.7 | 227.1 | 221.8 | 202.0 | 274.6 | 332 |
| 334 | 296.7 | 154.2 | 158.9 | 157.9 | 151.7 | 228.5 | 223.2 | 203.3 | 276.2 | 334 |
| 336 | 298.5 | 155.2 | 159.9 | 159.0 | 152.8 | 229.9 | 224.6 | 204.6 | 277.9 | 336 |
| 338 | 300.2 | 156.3 | 161.0 | 160.0 | 153.8 | 231.3 | 226.0 | 205.9 | 279.5 | 338 |
| 340 | 302.0 | 157.3 | 162.0 | 161.0 | 154.8 | 232.7 | 227.4 | 207.1 | 281.2 | 340 |
| 342 | 303.8 | 158.3 | 163.1 | 162.1 | 155.9 | 234.1 | 228.7 | 208.4 | 282.9 | 342 |
| 344 | 305.6 | 159.3 | 164.1 | 163.1 | 156.9 | 235.5 | 230.1 | 209.7 | 284.5 | 344 |
| 346 | 307.3 | 160.3 | 165.1 | 164.2 | 158.0 | 236.9 | 231.5 | 211.0 | 286.2 | 346 |
| 348 | 309.1 | 161.4 | 166.2 | 165.2 | 159.0 | 238.3 | 232.9 | 212.2 | 287.9 | 348 |
| 350 | 310.9 | 162.4 | 167.2 | 166.3 | 160.1 | 239.7 | 234.3 | 213.5 | 289.5 | 350 |
| 352 | 312.7 | 163.4 | 168.3 | 167.3 | 161.1 | 241.1 | 235.6 | 214.8 | 291.2 | 352 |
| 354 | 314.4 | 164.4 | 169.3 | 168.4 | 162.2 | 242.5 | 237.0 | 216.1 | 292.8 | 354 |
| 356 | 316.2 | 165.4 | 170.4 | 169.4 | 163.2 | 243.9 | 238.4 | 217.3 | 294.5 | 356 |
| 358 | 318.0 | 166.5 | 171.4 | 170.5 | 164.3 | 245.3 | 239.8 | 218.6 | 296.2 | 358 |
| 360 | 319.8 | 167.5 | 172.5 | 171.5 | 165.3 | 246.7 | 241.2 | 219.9 | 297.8 | 360 |
| 362 | 321.6 | 168.5 | 173.5 | 172.6 | 166.4 | 248.1 | 242.5 | 221.2 | 299.5 | 362 |
| 364 | 323.3 | 169.6 | 174.6 | 173.7 | 167.4 | 249.5 | 243.9 | 222.5 | 301.2 | 364 |
| 366 | 325.1 | 170.6 | 175.6 | 174.7 | 168.5 | 250.9 | 245.3 | 223.7 | 302.8 | 366 |
| 368 | 326.9 | 171.6 | 176.7 | 175.8 | 169.5 | 252.3 | 246.7 | 225.0 | 304.5 | 368 |
| 370 | 328.7 | 172.7 | 177.7 | 176.8 | 170.6 | 253.7 | 248.1 | 226.3 | 306.1 | 370 |
| 372 | 330.4 | 173.7 | 178.8 | 177.9 | 171.6 | 255.1 | 249.5 | 227.6 | 307.8 | 372 |
| 374 | 332.2 | 174.7 | 179.8 | 179.0 | 172.7 | 256.5 | 250.9 | 228.9 | 309.5 | 374 |
| 376 | 334.0 | 175.8 | 180.9 | 180.0 | 173.7 | 257.9 | 252.2 | 230.2 | 311.1 | 376 |
| 378 | 335.8 | 176.8 | 182.0 | 181.1 | 174.8 | 259.3 | 253.6 | 231.5 | 312.8 | 378 |
| 380 | 337.5 | 177.9 | 183.0 | 182.1 | 175.9 | 260.7 | 255.0 | 232.8 | 314.5 | 380 |
| 382 | 339.3 | 178.9 | 184.1 | 183.2 | 176.9 | 262.1 | 256.4 | 234.1 | 316.1 | 382 |
| 384 | 341.1 | 180.0 | 185.2 | 184.3 | 178.0 | 263.5 | 257.8 | 235.4 | 317.8 | 384 |
| 386 | 342.9 | 181.0 | 186.2 | 185.4 | 179.1 | 264.9 | 259.2 | 236.6 | 319.4 | 386 |
| 388 | 344.6 | 182.0 | 187.3 | 186.4 | 180.1 | 266.5 | 260.5 | 237.9 | 321.1 | 388 |
| 390 | 346.4 | 183.1 | 188.4 | 187.5 | 181.2 | 267.7 | 261.9 | 239.2 | 322.8 | 390 |
| 392 | 348.2 | 184.1 | 189.4 | 188.6 | 182.3 | 269.1 | 263.3 | 240.5 | 324.4 | 392 |
| 394 | 350.0 | 185.2 | 190.5 | 189.7 | 183.3 | 270.5 | 264.7 | 241.8 | 326.1 | 394 |
| 396 | 351.8 | 186.2 | 191.6 | 190.7 | 184.4 | 271.9 | 266.1 | 243.1 | 327.7 | 396 |
| 398 | 353.5 | 187.3 | 192.7 | 191.8 | 185.5 | 273.3 | 267.5 | 244.4 | 329.4 | 398 |
| 400 | 355.3 | 188.4 | 193.7 | 192.9 | 186.5 | 274.7 | 268.9 | 245.7 | 331.1 | 400 |
| 402 | 357.1 | 189.4 | 194.8 | 194.0 | 187.6 | 276.1 | 270.3 | 247.0 | 332.7 | 402 |
| 404 | 358.9 | 190.5 | 195.9 | 195.0 | 188.7 | 277.5 | 271.7 | 248.3 | 334.4 | 404 |
| 406 | 360.6 | 191.5 | 197.0 | 196.1 | 189.8 | 278.9 | 273.0 | 249.6 | 336.0 | 406 |
| 408 | 362.4 | 192.6 | 198.1 | 197.2 | 190.8 | 280.3 | 274.4 | 251.0 | 337.7 | 408 |

TABLE 12. MUNSON AND WALKER'S TABLE.—*Continued*
(Expressed in Milligrams)

| Cuprous Oxide ($Cu_2O$) | Copper (Cu) | Dextrose (*d*-Glucose) | Invert Sugar | Invert Sugar and Sucrose | | Lactose | Lactose and Sucrose | | Maltose | Cuprous Oxide ($Cu_2O$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 0.4 Gram Total Sugar | 2 Grams Total Sugar | $C_{12}H_{22}O_{11}+H_2O$ | 1 Lactose, 4 Sucrose | 1 Lactose, 12 Sucrose | $C_{12}H_{22}O_{11}+H_2O$ | |
| 410 | 364.2 | 193.7 | 199.1 | 198.3 | 191.9 | 281.7 | 275.8 | 252.3 | 339.4 | 410 |
| 412 | 366.0 | 194.7 | 200.2 | 199.4 | 193.0 | 283.2 | 277.2 | 253.6 | 341.0 | 412 |
| 414 | 367.7 | 195.8 | 201.3 | 200.5 | 194.1 | 284.6 | 278.6 | 254.9 | 342.7 | 414 |
| 416 | 369.5 | 196.8 | 202.4 | 201.6 | 195.2 | 286.0 | 280.0 | 256.2 | 344.4 | 416 |
| 418 | 371.3 | 197.9 | 203.5 | 202.6 | 196.2 | 287.4 | 281.4 | 257.5 | 346.0 | 418 |
| 420 | 373.1 | 199.0 | 204.6 | 203.7 | 197.3 | 288.8 | 282.8 | 258.8 | 347.7 | 420 |
| 422 | 374.8 | 200.1 | 205.7 | 204.8 | 198.4 | 290.2 | 284.2 | 260.1 | 349.3 | 422 |
| 424 | 376.6 | 201.1 | 206.7 | 205.9 | 199.5 | 291.6 | 285.6 | 261.4 | 351.0 | 424 |
| 426 | 378.4 | 202.2 | 207.8 | 207.0 | 200.6 | 293.0 | 287.0 | 262.7 | 352.7 | 426 |
| 428 | 380.2 | 203.3 | 208.9 | 208.1 | 201.7 | 294.4 | 288.4 | 264.0 | 354.3 | 428 |
| 430 | 382.0 | 204.4 | 210.0 | 209.2 | 202.7 | 295.8 | 289.8 | 265.4 | 356.0 | 430 |
| 432 | 383.7 | 205.5 | 211.1 | 210.3 | 203.8 | 297.2 | 291.2 | 266.6 | 357.6 | 432 |
| 434 | 385.5 | 206.5 | 212.2 | 211.4 | 204.9 | 298.6 | 292.6 | 268.0 | 359.3 | 434 |
| 436 | 387.3 | 207.6 | 213.3 | 212.5 | 206.0 | 300.0 | 294.0 | 269.3 | 361.0 | 436 |
| 438 | 389.1 | 208.7 | 214.4 | 213.6 | 207.1 | 301.4 | 295.4 | 270.6 | 362.6 | 438 |
| 440 | 390.8 | 209.8 | 215.5 | 214.7 | 208.2 | 302.8 | 296.8 | 272.0 | 364.3 | 440 |
| 442 | 392.6 | 210.9 | 216.6 | 215.8 | 209.3 | 304.2 | 298.2 | 273.3 | 365.9 | 442 |
| 444 | 394.4 | 212.0 | 217.8 | 216.9 | 210.4 | 305.6 | 299.6 | 274.6 | 367.6 | 444 |
| 446 | 396.2 | 213.1 | 218.9 | 218.0 | 211.5 | 307.0 | 301.0 | 275.9 | 369.3 | 446 |
| 448 | 397.9 | 214.1 | 220.0 | 219.1 | 212.6 | 308.4 | 302.4 | 277.2 | 370.9 | 448 |
| 450 | 399.7 | 215.2 | 221.1 | 220.2 | 213.7 | 309.9 | 303.8 | 278.6 | 372.6 | 450 |
| 452 | 401.5 | 216.3 | 222.2 | 221.4 | 214.8 | 311.3 | 305.2 | 279.9 | 374.2 | 452 |
| 454 | 403.3 | 217.4 | 223.3 | 222.5 | 215.9 | 312.7 | 306.6 | 281.2 | 375.9 | 454 |
| 456 | 405.1 | 218.5 | 224.4 | 223.6 | 217.0 | 314.1 | 308.0 | 282.5 | 377.6 | 456 |
| 458 | 406.8 | 219.6 | 225.5 | 224.7 | 218.1 | 315.5 | 309.4 | 283.9 | 379.2 | 458 |
| 460 | 408.6 | 220.7 | 226.7 | 225.8 | 219.2 | 316.9 | 310.8 | 285.2 | 380.9 | 460 |
| 462 | 410.4 | 221.8 | 227.8 | 226.9 | 220.3 | 318.3 | 312.2 | 286.5 | 382.5 | 462 |
| 464 | 412.2 | 222.9 | 228.9 | 228.1 | 221.4 | 319.7 | 313.6 | 287.8 | 384.2 | 464 |
| 466 | 413.9 | 224.0 | 230.0 | 229.2 | 222.5 | 321.1 | 315.0 | 289.2 | 385.9 | 466 |
| 468 | 415.7 | 225.1 | 231.2 | 230.3 | 223.7 | 322.5 | 316.4 | 290.5 | 387.5 | 468 |
| 470 | 417.5 | 226.2 | 232.3 | 231.4 | 224.8 | 323.9 | 317.7 | 291.8 | 389.2 | 470 |
| 472 | 419.3 | 227.4 | 233.4 | 232.5 | 225.9 | 325.3 | 319.1 | 293.2 | 390.8 | 472 |
| 474 | 421.0 | 228.3 | 234.5 | 233.7 | 227.0 | 326.8 | 320.5 | 294.5 | 392.5 | 474 |
| 476 | 422.8 | 229.6 | 235.7 | 234.8 | 228.1 | 328.2 | 321.9 | 295.8 | 394.2 | 476 |
| 478 | 424.6 | 230.7 | 236.8 | 235.9 | 229.2 | 329.6 | 323.3 | 297.1 | 395.8 | 478 |
| 480 | 426.4 | 231.8 | 237.9 | 237.1 | 230.3 | 331.0 | 324.7 | 298.5 | 397.5 | 480 |
| 482 | 428.1 | 232.9 | 239.1 | 238.2 | 231.5 | 332.4 | 326.1 | 299.8 | 399.1 | 482 |
| 484 | 429.9 | 234.1 | 240.2 | 239.3 | 232.6 | 333.8 | 327.5 | 301.1 | 400.8 | 484 |
| 486 | 431.7 | 235.2 | 241.4 | 240.5 | 233.7 | 335.2 | 328.9 | 302.5 | 402.4 | 486 |
| 488 | 433.5 | 236.3 | 242.5 | 241.6 | 234.8 | 336.6 | 330.3 | 303.8 | 404.1 | 488 |
| 490 | 435.3 | 237.4 | 243.6 | 242.7 | 236.0 | 338.0 | 331.7 | 305.1 | 405.8 | 490 |

*Procedure for the Reduction.* In general, the method consists in placing 25 ml. of each of the Fehling's solutions into a 400 ml. beaker. Add to this 50 ml. of the sugar solution to be tested or, if a smaller volume of sample is used, add sufficient water to bring to a total volume of 50 ml. It is essential that the total volume of the two Fehling's solutions and sample in the beaker comprise 100 ml. Cover with a watch glass and place over a burner which has been previously regulated so that the solution will come to a boil in exactly 4 min. Boil for 2 min. and filter immediately through a Gooch crucible prepared with acid and alkaline digested asbestos. Thoroughly wash the precipitated cuprous oxide in the crucible and determine the amount of copper reduced by one of the accepted methods. The reduction procedure is strictly empirical and all directions must be followed explicitly if the results are to be of any value.

**Quisumbing and Thomas Method.** Some of the difficulties and possible sources of error in the Munson and Walker method have been eliminated by the Quisumbing and Thomas method.[1] The main differences in the methods are the somewhat more concentrated alkaline tartrate solution and the method of heating for the copper reduction. The more concentrated alkaline tartrate solution is said to give better cuprous oxide crystals. The heating process involves heating the sugar sample and reagents for 30 min. at 80° C. Small differences in the heating time or temperature do not noticeably affect the final results. In addition, no reduction of copper occurs if sucrose is also present. This method lends itself better to routine work than the Munson and Walker method since much less personal attention is required in the reduction process.

*Reagents.*

1. *Copper Sulfate Solution.* Wash the crystals of copper sulfate ($CuSO_4 \cdot 5\,H_2O$) free from dust with water. Dissolve them in hot water to make a saturated solution. Determine the copper content electrolytically or by titration, and dilute the solution so that 25 ml. of it will contain 525 mg. of copper.
2. *Alkaline Tartrate Solution.* Prepare a saturated solution of sodium hydroxide and allow to stand for several days to permit the carbonates to settle out. Siphon off the clear supernatant solution and determine its concentration by titration with standard acid. Dissolve 173 grams of high grade Rochelle salts (sodium potassium tartrate) in water in

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[1] Quisumbing and Thomas, *J. Amer. Chem. Soc.*, **43**, 1503 (1921).

a 500 ml. volumetric flask. Add sufficient saturated sodium hydroxide solution to give 65 grams of sodium hydroxide and dilute to volume with water.

*Procedure for Reduction.* Pipette exactly 25 ml. each of the copper sulfate and the alkaline tartrate solutions into a 400 ml. beaker of about 9 cm. diameter. Add 50 ml. of the sugar solution, preferably containing 100–150 mg. of sugar. If a smaller volume of sugar sample is used, add sufficient water to bring to a total volume of 50 ml. It is essential that the total volume of Fehling's solutions and sample in the beaker comprise 100 ml. Cover the beaker with a watch glass and place in a water bath maintained at 80° C. A thermostatically controlled water bath is ideal. Digest for 30 min. and filter through an asbestos mat in a Gooch crucible as in the Munson and Walker method. Determine the reduced copper by one of the accepted methods. Quisumbing and Thomas recognized that, while the direct weighing of cuprous oxide was the quickest, it was liable to inaccuracy when solutions other than pure sugars were used, due to contamination with impurities. They determined the reduced copper values given in their table by an electrolytic method. Thus, for greatest accuracy, the reduced copper should be determined by either a volumetric or electrolytic method. From the amount of copper reduced, determine the amount of sugar present from the Quisumbing and Thomas table on page 173.

**Selection of Method for Determining Reduced Copper.** Munson and Walker determined the reduced copper by weighing the cuprous oxide and converting to metallic copper by the stoichiometrical factor. According to their statements, the method was checked against the electrolytic and thiosulfate methods and the accuracy of the curpous oxide procedure demonstrated. This has been questioned, however, by later investigators who have demonstrated the contamination of the cuprous oxide precipitate by organic decomposition products, even when pure sugars were analyzed.

As a result of the work of Hammond[1] and of Jackson and McDonald[2] it has been shown definitely that the Munson and Walker table (Table 12), in so far as it relates sugar to metallic copper, is in error by the amount of the contamination. For most accurate results, then, the reduced copper should be determined by

[1] Hammond, *J. Research of Natl. Bur. of Standards*, **24**, 579 (1940).

[2] Jackson and McDonald, *J. Assoc. Off. Agr. Chem.*, **24**, 767 (1941).

TABLE 13.* QUISUMBING AND THOMAS TABLE FOR CALCULATING DEXTROSE, LEVULOSE, INVERT SUGAR, LACTOSE, AND MALTOSE

(Expressed in Milligrams)

| Copper (Cu) | Cuprous Oxide ($Cu_2O$) | Dextrose (*d*-Glucose) | Levulose (*d*-Fructose) | Invert Sugar | Lactose | | Maltose | |
|---|---|---|---|---|---|---|---|---|
| | | | | | $C_{12}H_{22}O_{11}$ | $\cdot C_{12}H_{22}O_{11}\cdot H_2O\cdot$ | $C_{12}H_{22}O_{11}$ | $\cdot C_{12}H_{22}O_{11}\cdot H_2O$ |
| 10 | 11.1 | 4.8 | 5.3 | 5.0 | 7.7 | 8.1 | 9.4 | 9.9 |
| 20 | 22.5 | 9.5 | 10.5 | 10.1 | 15.5 | 16.3 | 18.8 | 19.8 |
| 30 | 33.8 | 14.3 | 15.8 | 15.2 | 23.2 | 24.4 | 28.2 | 29.7 |
| 40 | 45.0 | 19.1 | 21.2 | 20.3 | 30.9 | 32.5 | 37.6 | 39.6 |
| 50 | 56.3 | 24.0 | 26.5 | 25.4 | 38.7 | 40.7 | 47.0 | 49.5 |
| 60 | 67.6 | 28.9 | 31.9 | 30.6 | 46.4 | 48.8 | 56.4 | 59.4 |
| 70 | 78.8 | 33.7 | 37.2 | 35.7 | 54.0 | 56.9 | 65.8 | 69.3 |
| 80 | 90.1 | 38.7 | 42.6 | 40.9 | 61.7 | 65.0 | 75.2 | 79.2 |
| 90 | 101.3 | 43.6 | 48.0 | 46.1 | 69.5 | 73.2 | 84.6 | 89.1 |
| 100 | 112.6 | 48.6 | 53.4 | 51.3 | 77.2 | 81.3 | 94.0 | 99.0 |
| 110 | 123.8 | 53.5 | 58.8 | 56.5 | 85.0 | 89.5 | 103.4 | 108.9 |
| 120 | 135.1 | 58.5 | 64.3 | 61.8 | 92.7 | 97.0 | 112.8 | 118.8 |
| 130 | 146.4 | 63.5 | 70.7 | 67.0 | 100.4 | 105.7 | 122.2 | 128.7 |
| 140 | 157.6 | 68.6 | 75.2 | 72.3 | 108.2 | 113.9 | 131.6 | 138.6 |
| 150 | 168.9 | 73.7 | 80.7 | 77.6 | 116.0 | 122.0 | 141.0 | 148.5 |
| 160 | 180.1 | 78.8 | 86.2 | 82.9 | 123.7 | 130.1 | 150.4 | 158.4 |
| 170 | 191.4 | 83.9 | 91.7 | 88.3 | 131.4 | 138.3 | 159.8 | 168.3 |
| 180 | 202.6 | 89.1 | 97.2 | 93.7 | 139.1 | 146.4 | 169.2 | 178.2 |
| 190 | 213.9 | 94.2 | 102.8 | 99.1 | 146.9 | 154.6 | 178.8 | 188.1 |
| 200 | 225.2 | 99.4 | 108.4 | 104.4 | 154.6 | 162.7 | 188.2 | 198.0 |
| 210 | 236.4 | 104.6 | 114.0 | 109.8 | 162.3 | 170.9 | 197.6 | 207.9 |
| 220 | 247.7 | 109.9 | 119.6 | 115.2 | 170.0 | 179.0 | 207.0 | 217.8 |
| 230 | 258.9 | 115.1 | 125.2 | 120.6 | 177.8 | 187.2 | 216.4 | 227.7 |
| 240 | 270.2 | 120.4 | 130.8 | 126.1 | 185.5 | 195.3 | 225.8 | 237.6 |
| 250 | 281.5 | 125.7 | 136.4 | 131.6 | 193.2 | 203.4 | 235.2 | 247.5 |
| 260 | 292.7 | 131.0 | 142.1 | 137.1 | 201.0 | 211.6 | 244.6 | 257.4 |
| 270 | 304.0 | 136.4 | 147.8 | 142.6 | 208.8 | 219.8 | 254.0 | 267.3 |
| 280 | 315.2 | 141.7 | 153.5 | 148.2 | 216.5 | 227.9 | 263.4 | 277.2 |
| 290 | 326.5 | 147.1 | 159.2 | 153.7 | 224.2 | 236.0 | 272.8 | 287.1 |
| 300 | 337.8 | 152.6 | 165.0 | 159.3 | 232.0 | 244.2 | 282.2 | 297.0 |
| 310 | 349.0 | 158.0 | 170.7 | 164.9 | 239.7 | 252.3 | 291.6 | 306.9 |
| 320 | 360.3 | 163.5 | 176.5 | 170.5 | 247.5 | 260.5 | 301.0 | 316.8 |
| 330 | 371.5 | 168.9 | 182.3 | 176.1 | 255.3 | 268.7 | 310.4 | 326.7 |
| 340 | 382.8 | 174.5 | 188.1 | 181.8 | 263.0 | 276.8 | 319.8 | 336.6 |
| 350 | 394.0 | 180.0 | 193.9 | 187.4 | 270.7 | 285.0 | 329.2 | 346.5 |
| 360 | 405.3 | 185.5 | 199.7 | 193.1 | 278.4 | 293.1 | 338.6 | 356.4 |
| 370 | 416.6 | 191.1 | 205.5 | 198.8 | 286.2 | 301.3 | 348.0 | 366.3 |
| 380 | 427.8 | 196.7 | 211.4 | 204.5 | 293.9 | 309.4 | 357.4 | 376.2 |
| 390 | 439.1 | 202.3 | 217.3 | 210.2 | 301.6 | 317.5 | 366.8 | 386.1 |
| 400 | 450.3 | 208.0 | 223.2 | 216.0 | 309.4 | 325.7 | 376.2 | 396.0 |
| 410 | 461.6 | 213.7 | 229.1 | 221.8 | 317.1 | 333.8 | 385.6 | 405.9 |
| 420 | 472.9 | 219.4 | 235.0 | 227.6 | 324.9 | 342.0 | 395.0 | 415.8 |
| 430 | 484.1 | 225.1 | 240.9 | 233.4 | 332.6 | 350.1 | 404.4 | 425.7 |
| 440 | 495.4 | 230.8 | 246.9 | 239.2 | 340.4 | 358.3 | 413.8 | 435.6 |
| 450 | 506.6 | 236.6 | 252.9 | 245.0 | 348.1 | 366.4 | 423.2 | 445.5 |
| 460 | 517.9 | 242.4 | 258.9 | 250.9 | 355.9 | 374.6 | 432.6 | 455.4 |
| 470 | 529.1 | 248.1 | 264.9 | 256.8 | 363.6 | 382.7 | 442.0 | 465.3 |
| 480 | 540.4 | 250.8 | 270.9 | 262.7 | 371.3 | 390.9 | 451.4 | 475.2 |

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* From the Assoc. Off. Agr. Chem., "Methods of Analysis" (1940).

Table 14.* Hammond's Table for Calculating Dextrose, Invert Sugar Alone, Invert Sugar in the Presence of Sucrose (0.3, 0.4, and 2.0 Grams of Total Sugar), and Levulose†

| Copper (mg.) | Cuprous Oxide (mg.) | Dextrose (mg.) | Invert Sugar (mg.) | Invert Sugar and Sucrose | | | Levulose (mg.) |
|---|---|---|---|---|---|---|---|
| | | | | 0.3 g. of Total Sugar (mg.) | 0.4 g. of Total Sugar (mg.) | 2.0 g. of Total Sugar (mg.) | |
| 10 | 11.3 | 4.6 | 5.2 | 3.2 | 2.9 | — | 5.1 |
| 15 | 16.9 | 7.0 | 7.7 | 5.8 | 5.4 | — | 7.7 |
| 20 | 22.5 | 9.4 | 10.2 | 8.3 | 7.9 | 1.9 | 10.4 |
| 25 | 28.1 | 11.9 | 12.8 | 10.9 | 10.5 | 4.4 | 13.1 |
| 30 | 33.8 | 14.3 | 15.3 | 13.4 | 13.0 | 7.0 | 15.8 |
| 35 | 39.4 | 16.7 | 17.8 | 16.0 | 15.6 | 9.5 | 18.4 |
| 40 | 45.0 | 19.2 | 20.4 | 18.6 | 18.2 | 12.1 | 21.1 |
| 45 | 50.7 | 21.6 | 22.9 | 21.2 | 20.7 | 14.7 | 23.8 |
| 50 | 56.3 | 24.1 | 25.5 | 23.8 | 23.3 | 17.3 | 26.5 |
| 55 | 61.9 | 26.5 | 28.1 | 26.3 | 25.9 | 19.9 | 29.2 |
| 60 | 67.6 | 29.0 | 30.6 | 28.9 | 28.5 | 22.5 | 31.9 |
| 65 | 73.2 | 31.5 | 33.2 | 31.6 | 31.1 | 25.1 | 34.7 |
| 70 | 78.8 | 34.0 | 35.8 | 34.2 | 33.7 | 27.7 | 37.4 |
| 75 | 84.4 | 36.5 | 38.4 | 36.8 | 36.3 | 30.3 | 40.1 |
| 80 | 90.1 | 39.0 | 41.0 | 39.4 | 38.9 | 32.9 | 42.8 |
| 85 | 95.7 | 41.5 | 43.6 | 42.0 | 41.6 | 35.5 | 45.6 |
| 90 | 101.3 | 44.0 | 46.2 | 44.7 | 44.2 | 38.2 | 48.3 |
| 95 | 107.0 | 46.5 | 48.8 | 47.3 | 46.8 | 40.8 | 51.1 |
| 100 | 112.6 | 49.0 | 51.5 | 50.0 | 49.5 | 43.5 | 53.8 |
| 105 | 118.2 | 51.6 | 54.1 | 52.6 | 52.1 | 46.1 | 56.6 |
| 110 | 123.8 | 54.1 | 56.7 | 55.3 | 54.8 | 48.8 | 59.3 |
| 115 | 129.5 | 56.7 | 59.4 | 57.9 | 57.4 | 51.5 | 62.1 |
| 120 | 135.1 | 59.2 | 62.0 | 60.6 | 60.1 | 54.1 | 64.9 |
| 125 | 140.7 | 61.8 | 64.7 | 63.3 | 62.8 | 56.8 | 67.7 |
| 130 | 146.4 | 64.3 | 67.4 | 66.0 | 65.5 | 59.5 | 70.4 |
| 135 | 152.0 | 66.9 | 70.0 | 68.7 | 68.2 | 62.2 | 73.2 |
| 140 | 157.6 | 69.5 | 72.7 | 71.4 | 70.9 | 64.9 | 76.0 |
| 145 | 163.2 | 72.1 | 75.4 | 74.1 | 73.6 | 67.7 | 78.8 |
| 150 | 168.9 | 74.7 | 78.1 | 76.8 | 76.3 | 70.4 | 81.6 |
| 155 | 174.5 | 77.3 | 80.8 | 79.5 | 79.0 | 73.1 | 84.4 |
| 160 | 180.1 | 79.9 | 83.5 | 82.2 | 81.7 | 75.9 | 87.3 |
| 165 | 185.8 | 82.5 | 86.2 | 85.0 | 84.5 | 78.6 | 90.1 |
| 170 | 191.4 | 85.2 | 88.9 | 87.7 | 87.2 | 81.4 | 92.9 |
| 175 | 197.0 | 87.8 | 91.7 | 90.5 | 90.0 | 84.1 | 95.7 |
| 180 | 202.7 | 90.4 | 94.4 | 93.2 | 92.7 | 86.9 | 98.6 |
| 185 | 208.3 | 93.1 | 97.1 | 96.0 | 95.5 | 89.7 | 101.4 |
| 190 | 213.9 | 95.7 | 99.9 | 98.7 | 98.2 | 92.4 | 104.3 |
| 195 | 219.5 | 98.4 | 102.6 | 101.5 | 101.0 | 95.2 | 107.1 |
| 200 | 225.2 | 101.1 | 105.4 | 104.3 | 103.8 | 98.0 | 110.0 |
| 205 | 230.8 | 103.8 | 108.2 | 107.1 | 106.6 | 100.9 | 112.9 |

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* Hammond, *J. Research of Natl. Bureau of Stand.*, **24**, 579 (1940). Research Paper, R. P. 1301.

† The values in the table for concentrations of reducing sugar less than 20 mg. are extrapolated and should be used with caution and only for approximate determinations.

TABLE 14. HAMMOND'S TABLE.—*Continued*

| Copper (mg.) | Cuprous Oxide (mg.) | Dextrose (mg.) | Invert Sugar (mg.) | Invert Sugar and Sucrose | | | Levulose (mg.) |
|---|---|---|---|---|---|---|---|
| | | | | 0.3 g. of Total Sugar (mg.) | 0.4 g. of Total Sugar (mg.) | 2.0 g. of Total Sugar (mg.) | |
| 210 | 236.4 | 106.5 | 110.9 | 109.9 | 109.4 | 103.7 | 115.7 |
| 215 | 242.1 | 109.2 | 113.7 | 112.7 | 112.2 | 106.5 | 118.6 |
| 220 | 247.7 | 111.9 | 116.5 | 115.5 | 115.0 | 109.3 | 121.5 |
| 225 | 253.3 | 114.6 | 119.3 | 118.3 | 117.8 | 112.2 | 124.4 |
| 230 | 258.9 | 117.3 | 122.1 | 121.1 | 120.7 | 115.0 | 127.3 |
| 235 | 264.6 | 120.0 | 124.9 | 124.0 | 123.5 | 117.9 | 130.2 |
| 240 | 270.2 | 122.7 | 127.8 | 126.8 | 126.3 | 120 7 | 133.1 |
| 245 | 275.8 | 125.5 | 130.6 | 129.6 | 129.2 | 123.6 | 136.0 |
| 250 | 281.5 | 128.2 | 133.4 | 132.5 | 132.0 | 126.5 | 138.9 |
| 255 | 287.1 | 131.0 | 136.3 | 135.3 | 134.9 | 129.4 | 141.8 |
| 260 | 292.7 | 133.8 | 139.1 | 138.2 | 137.8 | 132.3 | 144.8 |
| 265 | 298.3 | 136.5 | 142.0 | 141.1 | 140.7 | 135.2 | 147.7 |
| 270 | 304.0 | 139.3 | 144.8 | 144.0 | 143.5 | 138.1 | 150.6 |
| 275 | 309.6 | 142.1 | 147.7 | 146.8 | 146.4 | 141.0 | 153.6 |
| 280 | 315.2 | 144.9 | 150.6 | 149.7 | 149.3 | 143.9 | 156.5 |
| 285 | 320.9 | 147.7 | 153.5 | 152.6 | 152.2 | 146.9 | 159.5 |
| 290 | 326.5 | 150.5 | 156.4 | 155.5 | 155.2 | 149.8 | 162.5 |
| 295 | 332.1 | 153.4 | 159.3 | 158.5 | 158.1 | 152.8 | 165.4 |
| 300 | 337.8 | 156.2 | 162.2 | 161.4 | 161.0 | 155.7 | 168.4 |
| 305 | 343.4 | 159.0 | 165.1 | 164.3 | 164.0 | 158.7 | 171.4 |
| 310 | 349.0 | 161.9 | 168.0 | 167.2 | 166.9 | 161.7 | 174.4 |
| 315 | 354.6 | 164.7 | 171.0 | 170.2 | 169.9 | 164.7 | 177.4 |
| 320 | 360.3 | 167.6 | 173.9 | 173.1 | 172.8 | 167.7 | 180.4 |
| 325 | 365.9 | 170.5 | 176.9 | 176.1 | 175.8 | 170.7 | 183.4 |
| 330 | 371.5 | 173.4 | 179.8 | 179.1 | 178.8 | 173.7 | 186.4 |
| 335 | 377.2 | 176.3 | 182.8 | 182.1 | 181.8 | 176.7 | 189.4 |
| 340 | 382.8 | 179.2 | 185.8 | 185.0 | 184.8 | 179.8 | 192.5 |
| 345 | 388.4 | 182.1 | 188.8 | 188.0 | 187.8 | 182.8 | 195.5 |
| 350 | 394.0 | 185.0 | 191.8 | 191.0 | 190.8 | 185.9 | 198.5 |
| 355 | 399.7 | 187.9 | 194.8 | 194.0 | 193.8 | 188.9 | 201.6 |
| 360 | 405.3 | 190.9 | 197.8 | 197.1 | 196.9 | 192.0 | 204.7 |
| 365 | 410.9 | 193.8 | 200.8 | 200.1 | 199.9 | 195.1 | 207.7 |
| 370 | 416.6 | 196.8 | 203.8 | 203.1 | 203.0 | 198.2 | 210.8 |
| 375 | 422.2 | 199.7 | 206.9 | 206.2 | 206.0 | 201.3 | 213.9 |
| 380 | 427.8 | 202.7 | 209.9 | 209.2 | 209.1 | 204.4 | 217.0 |
| 385 | 433.5 | 205.7 | 213.0 | 212.3 | 212.2 | 207.5 | 220.1 |
| 390 | 439.1 | 208.7 | 216.0 | 215.4 | 215.3 | 210.6 | 223.2 |
| 395 | 444.7 | 211.7 | 219.1 | 218.5 | 218.4 | 213.8 | 226.3 |
| 400 | 450.3 | 214.7 | 222.2 | 221.5 | 221.5 | 217.0 | 229.4 |
| 405 | 456.0 | 217.8 | 225.4 | 224.7 | 224.7 | 220.1 | 232.6 |
| 410 | 461.6 | 220.8 | 228.5 | 227.8 | 227.8 | 223.3 | 235.8 |
| 415 | 467.2 | 223.9 | 231.7 | 231.0 | 231.0 | 226.6 | 239.0 |
| 420 | 472.9 | 227.0 | 234.8 | 234.2 | 234.2 | 229.8 | 242.2 |
| 425 | 478.5 | 230.1 | 238.1 | 237.5 | 237.5 | 233.1 | 245.6 |
| 430 | 484.1 | 233.3 | 241.5 | 240.9 | 241.0 | 236.5 | 249.2 |

analysis and not by direct weighing of cuprous oxide and Hammond's table (Table 14) substituted for that of Munson and Walker when using the Munson and Walker reduction method. When using the Quisumbing and Thomas reduction method and determining the reduced copper by the electrolytic or volumetric thiosulfate method, the Quisumbing and Thomas table (Table 13) should be used.

**Direct Weighing of Cuprous Oxide.** (Strictly applicable only to the Munson and Walker method.) The quickest method is to filter the cuprous oxide through a dried and previously weighed Gooch crucible. After thorough washing, the crucible and contents are dried in a 100° C. oven for 30-min. intervals until constant weight is reached. The only precautions to observe in this method are to dry thoroughly yet prevent any oxidation of the easily oxidizable cuprous oxide, hence the drying for 30-min. periods. From the Munson and Walker table (Table 12), ascertain the milligrams of sugar corresponding to the weight of cuprous oxide precipitate obtained in the determination.

**Volumetric Thiosulfate Method for Copper.** Of the two common volumetric methods available for the determination of copper, this is the one usually preferred.[1] The reactions involved are similar to those previously discussed for the standardization of a thiosulfate solution against copper as a primary standard, page 104.

The method depends upon the oxidation and solution of the cuprous oxide giving a soluble ionizable cupric salt. The cupric ion when treated with potassium iodide in an acid medium is reduced, and a corresponding amount of iodide ion is oxidized to molecular iodine. The amount of iodine liberated is then titrated with standard 0.1 N sodium thiosulfate solution and from this value, the corresponding amount of copper or cuprous oxide is calculated.

$$3\,Cu_2O + 2\,HNO_3 \rightarrow 6\,CuO + 2\,NO + H_2O$$

$$CuO + 2\,HNO_3 \rightarrow Cu(NO_3)_2 + H_2O$$

$$2\,Cu(NO_3)_2 + 4\,KI \rightarrow Cu_2I_2 + I_2 + 4\,KNO_3$$

$$I_2 + 2\,Na_2S_2O_3 \rightarrow 2\,NaI + Na_2S_4O_6.$$

*Reagents.*

1. *A 1:1 nitric acid solution.* To a definite volume of water add an equal volume of concentrated nitric acid.

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[1] Peters, *J. Amer. Chem. Soc.*, **34**, 422 (1912).

2. *Standard sodium thiosulfate solution.* Standardized against copper as a primary standard (page 104). A 0.15–0.16 N solution is recommended.
3. *Sodium acetate solution.* Dissolve 574 grams of the trihydrate and dilute to a liter of solution.
4. *Potassium iodide solution.* Dissolve 40 grams of potassium iodide in 100 ml. of solution.
   *Starch indicator solution* (see p. 101).

*Procedure.* Set a short stem funnel on the opening of a 300 ml. Erlenmeyer flask roughly graduated into 20 ml. portions. Set the Gooch crucible containing the thoroughly washed cuprous oxide in the funnel and place a watch glass over the crucible. Dissolve the cuprous oxide with 5 ml. of 1:1 nitric acid directed under the watch glass with a pipette. Carefully wash with small quantities of water the watch glass, crucible, and funnel collecting the copper solution in the Erlenmeyer flask. Boil to expel the red fumes, add a slight excess of strong bromine water and boil until the bromine is completely driven off. Cool, and add 10 ml. of the sodium acetate solution which buffers the effect of the nitric acid and liberates some acetic acid. Add sufficient potassium iodide solution, slowly and with constant agitation, so that at the end of the titration the concentration of potassium iodide will be 4.0–4.5 grams per 100 ml.

Titrate with the standard thiosulfate solution until the brown color becomes faint. Add freshly prepared starch indicator solution and continue the titration until the blue starch iodide is just decolorized. Add approximately 2 grams of ammonium thiocyanate, thoroughly dissolve it in the solution, then continue the titration to the disappearance of the blue color. From the volume of standard thiosulfate solution used, calculate the equivalent weight of copper in milligrams and ascertain the corresponding weight of sugar from Hammond's table (Table 14) or the Quisumbing and Thomas table (Table 13), depending upon the reduction method used.

**Volumetric Potassium Permanganate Method for Copper.**[1] In this method, the curpous oxide is treated with a solution of ferric sulfate and acidified with strong sulfuric acid. The curpous ion is oxidized in the reaction and a corresponding quantity of ferric ion is reduced to the ferrous state. The ferrous iron is then titrated with a standard potassium permanganate solution until the solution acquires a just perceptible permanganate color.

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[1] Jackson and McDonald, *J. Assoc. Off. Agr. Chem.*, 24, 775 (1941).

$$Cu_2O + Fe_2(SO_4)_3 + H_2SO_4 \rightarrow 2\,CuSO_4 + 2\,FeSO_4 + H_2O$$

$$10\,FeSO_4 + 2\,KMnO_4 + 8\,H_2SO_4 \rightarrow 5\,Fe_2(SO_4)_3 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2O.$$

*Reagents.*

1. *Standard 0.15–0.16 N potassium permanganate solution.*
2. *A 4 N sulfuric acid solution.* To 500 ml. of water add 115 ml. of concentrated sulfuric acid and dilute to a liter with water.
3. *Ferric sulfate solution.* Dissolve either 55 grams of anhydrous ferric sulfate or 135 grams of ferric ammonium alum in water and dilute to a liter. The anhydrous ferric sulfate dissolves quite slowly. To 50 ml. of this solution add 20 ml. of 4 N sulfuric acid solution and titrate with the permanganate solution to the first perceptible color change. Use this titration figure as a zero-point correction in subsequent analytical titrations.

*Procedure.* Transfer the crucible containing the thoroughly washed asbestos pad with the curpous oxide precipitate to the beaker. Add 50 ml. of the ferric sulfate solution and disintegrate the asbestos pad, stirring thoroughly until all the curpous oxide has dissolved. Hold the beaker above the level of the eye and examine carefully for complete solution. (If desired, the crucible may now be left in the beaker until the completion of the titration. If not, remove the crucible from the solution with the aid of the stirring rod and wash the crucible free from the solution with water, collecting the washings in the beaker.) Add 20 ml. of the 4 N sulfuric acid solution and titrate with the standard permanganate solution to the same end-point as in the titration for the zero-point correction on the ferric sulfate solution. Deduct the zero-point correction from the titration figure obtained, calculate its equivalence in milligrams of copper, and ascertain the corresponding milligrams of sugar from Hammond's table or the Quisumbing and Thomas table, depending upon the reduction method used.

**Electrolytic Method for Copper Using a Rotating Anode.**

*Preparation of the Electrodes.* Place electrodes in concentrated nitric acid for 1 min., remove, and rinse with water. Next, place them in a nitric acid solution (1:3) for 10–15 min. Remove, rinse thoroughly with tap water, and then with distilled water. Rinse in acetone, place on a watch glass and dry for 5 min. at 100°–120° C. Then place the cathode piece in a desiccator to cool and obtain its weight, being careful that the cathode is not touched with the hand at any time.

*Procedure.* Transfer the washed asbestos mat from the crucible to the beaker with the aid of a glass rod. Rinse the crucible with 14 ml. of a nitric acid solution (1:1), catching the rinsings in the beaker. When the cuprous oxide precipitate has dissolved, dilute to a 100 ml. volume, heat to boiling, and boil approximately 5 min. to expel the oxides of nitrogen. Cool, filter into a 400 ml. tall form beaker and wash the filter with sufficient water to insure that the entire copper solution has passed into the filtrate. Dilute to a volume of 200 ml., add 1 drop of 0.1 N hydrochloric acid and mix thoroughly.

Attach the electrodes to the apparatus with the anode rotating within the cathode cylinder. Be certain that the electrodes cannot touch during rotation. Place the 400 ml. beaker, containing the sample, on the shelf of the setup and adjust the height so that the electrodes just do not touch the bottom of the beaker.

Start the motor that rotates the anode, connect the battery, and adjust the current in the range of 0.5–2 amperes. Electrolyze for 30 min., add sufficient water to raise the liquid level approximately 1 cm. and electrolyze for another 10 min. If the cathode shows no fresh deposit by the end of this time, the electrolysis is complete. If electrolysis is not complete, electrolyze for 15 min. and again test for the completion of the reaction. When the reaction is complete, stop the rotation of the anode and slowly lower the beaker at the same time, thoroughly washing the electrodes with a stream of distilled water from a wash bottle. Replace the beaker with one having distilled water and have the anode rotate for a few moments. Then stop the rotation, and disconnect the current. Remove the cathode, rinse it in acetone, place it on a watch glass, and dry for 5 min. at 110°–120° C. Cool in a desiccator and weigh. From the weight obtained ascertain the corresponding weight of sugar from Hammond's tables or the Quisumbing and Thomas table, depending upon the reduction method used.

**Other Methods.** The first quantitative copper reduction method employing Fehling's solution was a volumetric method. A modification of this method, the Lane-Eynon method,[1, 2] has

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[1] Lane and Eynon, *J. Soc. Chem. Ind.*, 42, 32T (1923).

[2] Fitelson, *J. Assoc. Off. Agr. Chem.*, 15, 624 (1932).

found wide application because it is rapid and easily adapted to routine control work.

The Folin-Wu sugar method[1] is a colorimetric method for the determination of small concentrations of sugar in solution. The basis of this method is the reduction of copper in an alkaline solution to cuprous oxide by the sugar. The cuprous oxide upon treatment with phosphomolybdic acid solution produces a blue color which is compared with a standard in a colorimeter. This method, adapted to the determination of lactose in milk, is given in detail on page 218.

The picric acid sugar method is a colorimetric method depending upon the reduction, in alkaline solution, of the salt of picric acid to the picramate by the sugar. An advantage of this method in the determination of small amounts of sucrose is that the hydrolysis of the sucrose to reducing sugars is accomplished in the same tube in which the determination is run, by a preliminary heating with the picric acid solution used in the test. The method was suggested by Willaman and Davison[2] for the determination of glucose and sucrose in corn syrup and, with modifications, for the determination of the various common sugars.

## STARCH ANALYSIS

The starch content of a product is usually obtained by hydrolyzing the starch to glucose and determining this sugar by any of the copper reduction methods. The amount of glucose found multiplied by the appropriate factor will give the amount of starch originally present. An excellent résumé on methods for the estimation of starch is given by Sullivan.[3]

**Starch—Direct Acid Hydrolysis Method.** This method is applicable to starchy products (raw starch, potatoes, etc.) relatively free from pentosans and other carbohydrate materials which will undergo hydrolysis upon boiling with acid. The sample is washed with water to remove any soluble carbohydrates present. Complete hydrolysis of the starch to glucose is effected by boiling with approximately 20 per cent hydrochloric acid. The glucose is then determined by the Munson and Walker or Quisumbing and Thomas copper reduction methods and from this the amount of starch may be calculated with the aid of the factor 0.90.

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[1] Folin and Wu, *J. Biol. Chem.*, 41, 367 (1920).

[2] Willaman and Davison, *J. Agr. Res.*, 28, 479 (1924).

[3] Sullivan, *Ind. Eng. Chem., Anal. Ed.*, 7, 311 (1935).

*Procedure.* Weigh a sample representing 2.5–3.0 grams of the dry material into a beaker, add 50 ml. of cold water, and stir at intervals for 1 hour. Filter and wash with 250 ml. of cold water. Transfer the residue to a 500 ml. Erlenmeyer flask with 200 ml. of water and 20 ml. of hydrochloric acid (sp. gr. 1.125). Attach a reflux condenser to the flask and digest at the boiling temperature for 2.5 hours. Cool, transfer to a 250 ml. volumetric flask and nearly neutralize with strong sodium hydroxide solution (make alkaline to litmus with the sodium hydroxide, then add dilute hydrochloric acid until just acid to litmus). The sugar solution should be but slightly acid so that no appreciable amount of the alkali of Fehling's solution will be neutralized later in the copper reduction procedure. On the other hand, it must be slightly acid to prevent tautomeric changes and decomposition of the sugar present. Bring to the mark, mix thoroughly, and filter, collecting the filtrate in a clean dry flask.

Determine the glucose present in an aliquot of the filtrate by either the Munson and Walker or Quisumbing and Thomas copper reduction methods. The size aliquot to use will depend upon the product being analyzed. An aliquot should be taken so that the amount of glucose contained in it will fall somewhere near the center of the table giving the corresponding reduced copper values. The amount of glucose found multiplied by 0.90 will give the amount of starch. The method will be in error if substances other than starch are present which will give reducing sugars upon hydrolysis.

**Starch—Enzyme Hydrolysis Method.** Products containing starch along with pentosans and other carbohydrate materials require a somewhat more complicated method of analysis.[1] After removing soluble carbohydrates present by thorough washing with water, the sample is subjected to hydrolysis by the enzyme diastase. Since this enzyme is specific for starch, only the starch is hydrolyzed to the soluble disaccharide maltose, which is separated by filtration from the interfering substances. The maltose upon boiling with hydrochloric acid is converted to glucose which is then determined as in the direct acid hydrolysis method.

## MOISTURE

Numerous methods for the quantitative determination of moisture are available. The choice of method to use for a specific product will depend upon several factors: (1) form in which water is present, (2) nature of the product analyzed (whether easily oxidized or decomposed), (3) the relative amount of water present in the product, (4) rapidity of the determination, (5) the accuracy desired, and (6) the cost of the equipment required

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[1] Assoc. Off. Agr. Chem., "Methods of Analysis," 5th Ed. (1940), pp. 359–360.

Agricultural and biological material may contain water in different forms. The most common form is free or absorbed water which is readily determined by any of the moisture methods. Many products also contain adsorbed or colloidally bound water. Adsorbed water varies in the tightness with which it is held by different products, consequently moisture methods vary in the amount of the colloidally bound water which they will determine. Water of crystallization and mechanically occluded water may also be present in some materials. These forms of water may or may not be determined completely by the various moisture methods.

The nature of the product analyzed must be considered in selecting a moisture method. Excessive heating of products high in sugar may cause caramelization or decomposition of the sugar with the loss of the elements of water. Lipid materials oxidize in air at elevated temperatures and so samples containing fats may gain in weight when heated. Excretory products of animals contain substances which decompose readily into volatile constituents (ammonia, etc.) with heat. Tobacco also contains substances readily decomposed by heat. Consequently moisture methods which involve a high temperature or long heating period cannot be used on these products without introducing an error.

Materials high in moisture (green forage crops, vegetables, fruits, etc.) are usually dried rapidly to an "air-dry" condition at a temperature not exceeding 70°–80° C., with or without air circulation. That is, the product is reduced from a high moisture content which would rapidly cause spoilage to a moisture content which is in approximate equilibrium with atmospheric humidity, and which will inhibit spoilage by the action of microorganisms or enzymes. Normally, a relatively large sample of the green product is air-dried without previous grinding or appreciable disintegration and the loss of moisture determined. The air-dried sample is then ground to the required fineness and the moisture determined by one of the usual moisture methods. Certain methods, such as the distillation methods and methods based on the interaction of a chemical with water are especially adapted to the determination of water in products with low moisture contents.

In commercial routine analyses, it is frequently necessary to obtain moisture contents of products in a relatively short time.

Furthermore, methods requiring a longer time tie up a proportionately greater quantity of equipment and require more of the operators time. Methods vary in the time required for a determination from a few minutes to several weeks. Thus, the importance of selecting the proper method is obvious.

The different forms of water (absorbed, colloidally bound, mechanically occluded, water of crystallization) vary in the tenacity by which they are held in various products. For this reason, depending upon the forms of water present, the various moisture methods determine more or less of the "moisture" in the product. This has necessitated the adoption of standard or official methods for most agricultural and biological products. Whenever possible, these standard methods should be used if accurate results are desired. If only comparative results are desired, moisture methods, other than the standard ones, are satisfactory.

Moisture methods which involve oven drying require a sensitive analytical balance and an electrically heated thermostatically controlled vacuum oven or drying oven. Electrical methods involve more or less complicated and expensive electrical equipment. Distillation methods require the least expensive apparatus of all, in that only a balance of low sensitivity, and a distillation setup are necessary. Methods based on the interaction of a chemical and water also require relatively inexpensive equipment.

From the foregoing, it is evident that moisture determinations are empirical methods, since the various moisture methods employed determine more or less of the water present in the product. In other words, the conditions of the method govern to some extent the amount of moisture obtained. Thus, it is necessary to specify the method used along with the moisture percentage, e.g., 13.5 per cent moisture—determined in a vacuum oven at 100° C.; or 13.5 per cent moisture—determined by heating for 2 hours in an air-oven at 135° C.; or 13.5 per cent moisture—determined by the toluene distillation method.

## DRYING METHODS

Temperature and pressure govern the amount of water obtained by drying methods. As a result, drying methods involve the use of heat alone, heat and reduced pressure, or drying agents and reduced pressure.

**Vacuum Oven Method.** The early moisture methods involved drying a weighed sample to constant weight at the temperature of boiling water (approximately 100° C.). Substances which oxidized or decomposed upon heating at 100° C. were dried to constant weight at a lower temperature (70°–80° C.). A fairly long drying time was required in many instances. In an attempt to reduce the amount of decomposition and hasten the speed of drying, samples were dried in a vacuum oven under reduced pressure. However, upon comparison of the results obtained by drying a material at 100° C., with and without a vacuum, it was found that material dried in a vacuum gave a higher moisture percentage than when dried at the same temperature without a vacuum (Table 15).

TABLE 15. PERCENTAGES OF MOISTURE OBTAINED BY DIFFERENT DRYING METHODS

| Material | Method of Drying | | |
|---|---|---|---|
| | 100° C. in Vacuum | 70° C. in Vacuum | 100° C. Without Vacuum |
| Wheat flour | 12.62 | 12.03 | 11.11 |
| Hay | 7.30 | 6.51 | 6.34 |
| Dried string beans | 6.98 | 6.68 | 5.49 |

Consistency of results in replicate analyses is found to be greater when drying with a vacuum than when drying without a vacuum. Consequently the vacuum oven method is being accepted more and more as the standard official drying method.

*Procedure.* Dry an aluminum dish (approximately 50 mm. in diameter and 40 mm. deep) equipped with a tight fitting cover. Cool in a desiccator and weigh. Transfer approximately 2 grams of the sample to the dish, cover, and weigh. (Weighing an exactly 2.000 gram sample into the dish simplifies future calculations.) Remove the cover and place it loosely on the dish so that there is a one-fourth inch opening on one side between the cover and the dish. Place in the oven and dry for 5 hours at 100° C. with a pressure not to exceed 50 mm. of mercury. Immediately upon opening the oven, tap the dish cover thereby tightly closing the dish and remove to a desiccator. Cool and weigh. Continue the drying for one-hour intervals until constant weight is obtained and calculate the percentage of moisture present in the sample.

*Remarks.* Moisture in dehydrated vegetable and fruit products is determined by drying a 2.000 gram sample, ground to pass through a 30-mesh screen for 6 hours at 70° C. in a vacuum oven, with a pressure not to exceed 100 mm. of mercury.

Many substances are very hygroscopic when dried, so that covering the dish immediately upon opening the oven prevents the absorption of any moisture by the dry sample. The dish and contents should be weighed as soon as they have cooled in the desiccator. Some dried materials are better desiccants than those used in the desiccator and will pick up moisture in the desiccator even when in a closed dish.[1]

**Drying at Room Temperature in a Vacuum Desiccator.** Moisture in products containing substances which decompose or volatilize on heating cannot be determined by oven drying methods. Moisture in such products may be determined by drying at room temperature in a vacuum over a drying agent. This method is not employed unless necessary, due to the time required in making a determination and the amount of equipment tied up if many moisture determinations are involved.

*Procedure.* Weigh accurately an approximately 2 gram sample of the material into a dried and weighed moisture dish. Remove the cover and place the dish and cover in a vacuum desiccator freshly charged with 200 ml. of concentrated sulfuric acid. Attach the desiccator to a vacuum pump and exhaust to a pressure of not more than 10 mm. of mercury. Gently rotate the desiccator 4 to 5 times during the first 12 hours and let stand for 24 hours or longer. Break the vacuum by allowing air which previously has passed through concentrated sulfuric acid to come into the desiccator. Open the desiccator, place the cover on the dish, and weigh. Return the dish and cover to another desiccator freshly charged with concentrated sulfuric acid and continue the drying as before, opening the desiccator and weighing at definite intervals until constant weight is obtained. The loss in weight is taken as moisture.

*Remarks.* This method is used to determine the moisture content of feces and manures from which ammonia would volatilize if heated. It is also a standard method for determining the moisture content of tobacco which will lose nicotine and other volatile substances on heating. For tobacco, vacuum drying for a week over a good neutral or alkaline desiccant, such as magnesium perchlorate, calcium sulfate, or porus barium oxide, is recommended as the standard method for calibration.[2] Animal excreta are dried over concentrated sulfuric acid and weighed at weekly intervals until constant weight is attained.

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[1] Smith and Mitchell, *Ind. Eng. Chem.*, **17**, 180 (1925).

[2] Cone and Davis, *Ind. Eng. Chem., Anal. Ed.*, **9**, 219 (1937).

## DISTILLATION METHOD

Drying methods determine water indirectly by loss in weight during drying. The distillation method determines moisture directly by distilling the water and measuring the volume of water obtained. The method is especially valuable for determining water in products with low moisture contents.

Several advantages of the distillation method over drying methods are evident. The rate of dehydration may be followed visually and the completion of the determination is evident when no more water distills. A constant temperature of dehydration is maintained indefinitely without any trouble or the use of complicated apparatus. Oxidation of fats and decomposition of substances high in sugar are prevented. No expensive or complicated apparatus is required and neither is a highly specialized technique required. The method is readily adapted to routine control work and is much more rapid than oven drying methods, usually requiring about an hour for a determination.

**Bidwell-Sterling Moisture Method.**[1] This is the most commonly used distillation method (apparatus illustrated in Fig. 40). The weighed sample is covered with toluene and heated. The boiling point of toluene is slightly higher than that of water, so that upon boiling, the toluene and water distill over, are condensed and drop into a graduated collection tube. The water being heavier sinks to the bottom of the tube while the toluene continuously flows back into the distillation flask. When all the water has distilled over, the volume of water is read from the graduations on the collection tube. A constant distillation temperature is maintained throughout at the boiling temperature of toluene (approximately 111° C.).

*Procedure.* Weigh into a 300 ml. Erlenmeyer flask a sample which will give 2–5 ml. of water. If bumping is likely to occur, cover the bottom of the flask with dry sand before adding the sample. Add sufficient toluene to cover the sample completely (approximately 75 ml.). Connect the flask to the side arm of the Bidwell-Sterling tube as shown in Fig. 40. Pour toluene through the condenser until the collecting tube is filled. Heat the flask to boiling and distill slowly (about 2 drops per second) until most of the water has come over. Then increase the distillation rate to 4 drops per second until no more water comes over. Wash down the condenser with toluene. If water droplets adhere to the condenser, brush down with a burette brush saturated with toluene, at the same time pouring toluene through the top of the condenser. Continue the distillation for a short time to determine if any more water is coming over. If so, continue the distillation until no more water comes over and repeat the washing process. Remove the flame and allow the collecting tube to come to room temperature. If drops of water adhere to the sides of the collecting tube, force them down by means of a band of rubber tubing slipped over the end of a glass stirring rod. Read the volume of water distilled and, assuming its specific gravity to be 1.0, calculate the percentage of water present in the sample.

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[1] Bidwell and Sterling, *Ind. Eng. Chem.*, **17**, 147 (1925).

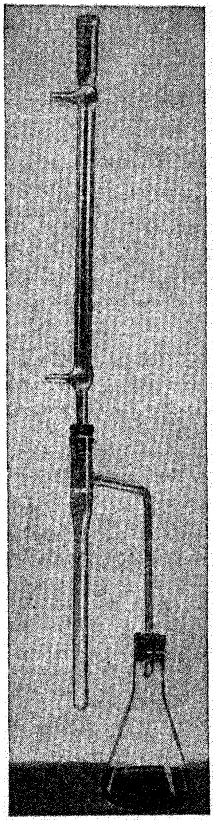

FIG. 40. Toluene Distillation Apparatus for the Determination of Moisture.

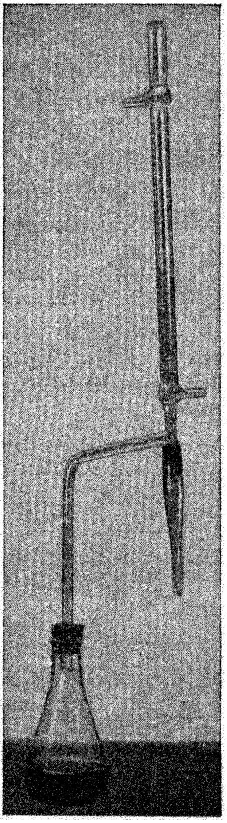

FIG. 41. Modified Toluene Distillation Apparatus.

*Remarks.* The main difficulty experienced in this determination is in having water droplets sticking to the sides of the condenser and the collecting tube. To eliminate this as much as possible, it is absolutely essential that the apparatus be *scrupulously clean* and *dry* before use. The apparatus should be washed thoroughly with soap and water, then with cleaning solution, rinsed thoroughly and dried over night before use.

A slight modification of the setup has been found useful in eliminating difficulties experienced in having water suspended in and sticking to the sides of the collecting tube. This modification is illustrated in Fig. 41. The side arm is made a part of the condenser unit. The collecting tube is simply a graduated tube attached to the condenser unit by means of a stopper. At the completion of the determination, the collecting tube is disconnected and centrifuged. In this way all the water is quickly and completely thrown to the bottom of the tube where its volume may be read.

It may be advantageous to substitute benzene or xylol in the moisture determination on different products by the distillation method. Thus, in the analysis of dehydrated fruit and vegetable products, benzene has been recommended in preference to toluene if the moisture results are to be comparable with those obtained by drying at 70° C. in a vacuum oven.

## GAS PRODUCTION METHOD

**Calcium Carbide Method.** This is a simple rapid moisture method requiring no elaborate apparatus. The method is based upon the reaction of calcium carbide with water to give acetylene. The amount of acetylene may be determined in one of three ways: (1) by the loss in weight of the mixture after the reaction has occurred, (2) by collecting the acetylene gas and measuring its volume, or (3) by determining the pressure developed by the acetylene when the reaction occurs in a closed system.

The method has been suggested for determining moisture on a variety of products. McNeil[1] indicated that the method was applicable to the determination of moisture in soap, leather, powder, sawdust, vanilla beans, flour, butter and fruit juices. Blish and Hites[2] report that the total flour moisture may be estimated with a degree of accuracy sufficient for most purposes in 5 min. by the calcium carbide procedure which they describe.

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[1] McNeil, U. S. Dept. Agr., *Cir. 97* (1912).

[2] Blish and Hites, *Cereal Chem.*, **7**, 99 (1930).

## TITRATION METHOD

**Fischer Volumetric Method.** This relatively new moisture method was proposed by Fischer[1] in 1935. The method consists in titrating the sample with a methanol solution of iodine, sulfur dioxide, and pyridine, to the appearance of the free iodine color. As long as water is present in the solution, the iodine is consumed.

According to Smith, Bryant and Mitchell[2] the reactions involved are:

$$I_2 + SO_2 + 3\,C_5H_5N + H_2O \rightarrow 2\,(C_5H_5N \cdot HI) + C_5H_5NOSO_2$$
$$C_5H_5NOSO_2 + CH_3OH \rightarrow C_5H_5N(HCH_3SO_4).$$

The original method has been improved in several ways.[3] Instead of titrating directly with the iodine solution, it has been found that a sharper end point is obtained if an excess of the iodine solution is added and the excess iodine back titrated with a standard methanol-water solution. Furthermore, the determination of the end point potentiometrically increases the precision of the method to an appreciable degree. The standard methanol solution of iodine, sulfur dioxide, and pyridine may be prepared in the laboratory or purchased from chemical supply houses.

The Fischer method has been applied successfully to the determination of water in: alcohols, esters, fats, waxes, Fullers earth, cellulose, glue, sugar, ketchup, honey and dehydrated foods. The results obtained with this method have been found to agree closely with those obtained by other accepted moisture methods. This method is coming into wide use because of its accuracy and saving in time.

## ELECTRICAL METHODS

Electrical methods for the determination of moisture operate upon two different principles: (1) dielectric and (2) conductivity. These methods will be discussed briefly as to general procedure and the reader is referred to the literature references for detailed information.

**Dielectric Method.** A description of this method and its use for the determination of moisture in flour is given by Coleman.[4] Water has a dielectric constant of 80, whereas starches, proteins, etc., found in cereals have dielectric constants of less than 10. By

[1] Fischer, *Angew. Chem.*, 48, 394 (1935).

[2] Smith, Bryant, and Mitchell, *J. Am. Chem. Soc.*, 61, 2407 (1939).

[3] Almy, Griffin, and Wilcox, *Ind. Eng. Chem., Anal. Ed.*, 12, 392 (1940).

[4] Coleman, *Cereal Chem.*, 8, 317 (1931).

determining this property on samples in standard metal condensers, dial readings may be obtained which can be converted into percentage of moisture from a graph previously constructed by plotting dial readings against percentages of moisture. The values obtained in constructing the graph are obtained on samples with known moisture contents.

The method has the advantage of making a moisture determination rapidly. The method as applied to grain is still somewhat in the experimental stage and does not give results of high accuracy compared to the other moisture methods.

**Conductivity Method.** The determination of moisture by this method depends upon the change in resistance to the passage of an electric current by variations in moisture present in the sample. The measurement of resistance is based on Ohm's law which states that the strength of a current is equal to the electromotive force divided by the resistance. The electrical resistance of wheat with 13 per cent moisture is approximately 7 times as great as that of wheat with 14 per cent of moisture and 50 times as great as wheat with 15 per cent moisture.

The Tag-Happenstahl moisture meter has been applied successfully to the determination of moisture in grains.[1] This apparatus consists essentially of two electrodes in the form of corrugated rolls which are rotated toward each other at a definite speed. The grain to be tested is fed in a layer one kernel deep between the revolving rolls. The resistance reading obtained is the resultant of the resistance for all the individual grains passing between the electrodes. By plotting readings obtained on samples of known moisture content against the corresponding moisture percentages, a graph can be constructed which will permit the conversion of any instrument reading to its corresponding moisture percentage.

Temperature changes influence electrical conductivity measurements so that a correction is necessary if determinations are made at temperatures other than the one used for calibrating the instrument. For most cereals, this appears to be a straight linear correction of 0.04 per cent per degree change in temperature.

Approximately 1 min. is required for the entire determination. Results obtained by this method agree well with those obtained by other accepted methods.

## DENSITY METHODS

Refractive indices and specific gravities of solutions vary with concentrations of the solute and so may be used as an indirect measure of the water content of the solution. These methods are used widely for the determination of moisture in sugar syrups. A detailed description of these methods as applied to the determination of moisture in maple syrup is given on page 236.

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[1] Coleman, *Cereal Chem.*, 8, 328 (1931).

## MINERAL ANALYSIS

Mineral elements are found in agricultural and biological material in organic and inorganic combinations. Inorganic salts, such as the phosphates, carbonates, chlorides, sulfates, and nitrates of sodium, potassium, and calcium, are common. Salts of organic acids, such as malic, oxalic, acetic, pectic, etc., may also be present. In addition, certain of the mineral elements may be built into complex organic molecules.

The nature and amount of the various mineral combinations that occur in many agricultural and biological products are usually difficult to determine. Ashing the material to eliminate all organic matter changes the nature of many of the combinations. In salts of organic acids, the organic radical is destroyed and the metallic elements form oxides or combine with other negatively charged radicals to form phosphates, sulfates, nitrates, or chlorides. Elements such as sulfur and phosphorus, frequently built into complex organic molecules, are oxidized to sulfates and phosphates. From this it is evident that ashing disrupts many mineral combinations and then an analysis of the ash will not give a true picture of the minerals as they are present in the original product. More techniques to accomplish this would be desirable.

### DETERMINATION OF ASH

**Straight Ash by Combustion.** This method consists in oxidizing all organic matter in a weighed sample of the material by incineration and determining the weight of the ash remaining.

*Procedure.* Weigh accurately a sample of the material into a previously ignited and weighed porcelain or platinum crucible. If a solid material is analyzed, a 2 gram sample is usually weighed out. If liquid, a larger sample, 5–10 grams (5–10 ml. if the specific gravity is known) or larger, is used. Liquid samples must be dried before ignition. Carefully ignite the sample over a burner and heat until the sample is thoroughly charred. Transfer the crucible and contents to a muffle furnace held at a dull red heat (550°–600° C.) and continue the ashing process until the ash has a gray-white appearance. Cool in a desiccator and weigh. Reheat in the muffle furnace for one-hour intervals until a constant weight is obtained. Calculate the percentage of ash.

Sugar products and plant materials rich in carbohydrates are ashed at a somewhat lower temperature. Two procedures are available for ashing. In one, the sample is ashed at 525° C. until a white ash is obtained. The ash is moistened with water, dried on a steam bath, then on a hot plate, and re-ashed in a muffle furnace at 525° C. to constant weight. In the other procedure, the sample is charred and then treated with water to dissolve the soluble salts. These are filtered off through an ashless filter paper. The filter paper and residue is ignited to a white ash. The filtrate is then added to the ash, evaporated to dryness, and ignited at 525° C. to constant weight.

Samples high in phosphates, or containing lead, arsenic, or antimony should not be ashed in platinum ware since they cause platinum to become brittle.

*Remarks.* Certain precautions are necessary in order to obtain accurate results. The rate of incineration must be adjusted so that there is no mechanical loss of ash during the process. The temperature of incineration is very important. Too high a temperature may cause the volatilization of certain elements (particularly K, Na, S, Cl and P) and may also cause the mineral matter to melt and fuse. Loss of these elements, even at low ashing temperatures, is frequently guarded against by the addition of acids to prevent loss of positive elements, and alkali to prevent loss of negative elements. When fusion occurs in the presence of unoxidized matter, the fused ash may surround and completely enclose or occlude some of the unoxidized material. Such occluded matter is then protected from further oxidation by conditions normally used in ashing, and the resulting ash will be too high.

The temperature of ashing is also important in that certain inorganic compounds do not lose their water of hydration at ashing temperatures of 500°–550° C.[1] Furthermore, ashing temperature influences the decomposition of carbonates to the oxides.[2] For example, potassium carbonate decomposes only slightly below 700° C., precipitated calcium carbonate decomposes considerably between 600°–650° C., and magnesium carbonate between 300°–400° C. However, magnesium and calcium carbonate are more stable to heat in the presence of potassium carbonate due to the formation of complex carbonates, or mass action effect, or both. In general, it is advisable to follow the specific ashing procedure recommended for a particular product if such a procedure is available.

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[1] Wichmann, *J. Assoc. Off. Agr. Chem.*, 25, 484 (1942).

[2] Wichmann, *J. Assoc. Off. Agr. Chem.*, 24, 441 (1941).

Ashing may be conducted entirely over a burner. Under these conditions, carbon may be deposited on the crucible or dish and, in addition, the temperature of ashing cannot be controlled accurately. Care should be exercised that only the oxidizing portion of the burner flame hits the crucible or dish, so that carbon is not deposited. Incineration in a muffle furnace with an automatic temperature control is preferable and eliminates the potential difficulties experienced in ashing over a burner.

If samples are started in a cold muffle furnace, no preliminary incineration is necessary. If, however, the muffle is at the temperature required for ashing, the samples should be incinerated previously over a burner so that the bulk of the organic matter is consumed before being placed in the furnace, thereby preventing too rapid incineration and possible mechanical loss of ash. With no ventilation in the rear of the muffle furnace, samples should not be placed in the areas 1 inch from the rear wall and 3 inches from the oven door, due to incomplete combustion in these areas. With through ventilation, the ashing area may be extended 1½ inches nearer to the front of the muffle furnace.

Freedom of the ash from carbon should not be used as a measure of complete ashing according to St. John.[1] This investigator found the amount of carbon remaining varied with the temperature of ashing and with the type of plant or animal material being ashed. In many instances, a material amount of carbon remained in the ash prepared at 700° C. However, the total relative weight of carbon in the ash was estimated to be very small.

**Modified Ash Methods.** The complete incineration of organic matter by the straight ash method requires several hours. This time may be reduced somewhat and a more complete combustion obtained, if the material to be ashed is distributed over a greater surface permitting a more intimate contact of the material with oxygen during the combustion process.

**A. Use of Sand.** Mixing the sample with sand distributes the material over a larger surface area and gives a porous mass, which permits oxygen to come into contact with the entire sample during combustion. As a result, oxidation of the organic matter is more readily accomplished and the time for complete combustion shortened.

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[1] St. John, *J. Assoc. Off. Agr. Chem.*, **25**, 969 (1942).

*Procedure.* A convenient amount of pure sand, 2–5 grams, is placed in the crucible or dish and heated to constant weight at the ashing temperature. The sample is then weighed into the crucible or dish and thoroughly mixed with the sand by means of a glass rod. The ashing is then conducted in the same manner as that for the straight ash. This procedure is especially useful in ashing samples in the liquid state, such as milk.

**B. Glycerol-alcohol Method.** The sample mixed with the glycerol-alcohol reagent forms a porous cake when ignited. The glycerol-alcohol reagent is completely oxidized in the process and so does not contribute to the final ash.

*Reagent.*

1. *Glycerol-alcohol Reagent.* A mixture of equal volumes of glycerol and ethyl alcohol.

*Procedure.* The sample is weighed into a previously ignited and weighed crucible. Sufficient glycerol-alcohol reagent is added to saturate the sample. Intimately mix the sample with the reagent using a glass rod and wipe off the glass rod with a small piece of ashless filter paper, which is then placed on top of the mixture. Ignite the filter paper and allow the mixture to burn until the flame dies out. The crucible and contents may then be placed in the muffle furnace and the ashing completed as in the straight ash.

**Extraction Method.** The extraction of minerals from a sample by the use of water followed by a conductivity measurement on the extract has been suggested as a means of determining the amount of mineral matter or ash. This method, suggested because it is less time consuming than the combustion methods, has not been used widely. Bailey,[1] in an application of this method to the determination of total ash in flour, found that the results obtained compared favorably with those obtained by the combustion method. However, the temperature and time of extraction must be carefully controlled in order to obtain good results.

The extraction of certain specific mineral elements from samples containing a number of other minerals is an important technique in quantitative analysis. Lead may be extracted from maple syrup in a relatively pure form by the use of dithizone.[2] In an analogous manner, copper, aluminum and other metallic elements may specifically be extracted from solution.

[1] Bailey, *J. Assoc. Off. Agr. Chem.*, 4, 456 (1921).

[2] Perlman, *J. Assoc. Off. Agr. Chem.*, 20, 622 (1937); *Ind. Eng. Chem., Anal. Ed.*, 10, 134 (1938).

# PART VI

# ANALYSIS OF AGRICULTURAL PRODUCTS

## CHAPTER XI

## FEEDSTUFFS

The analysis of a feedstuff usually involves what is known as a "proximate analysis." Such an analysis determines the percentages of water, crude fat or ether extract, ash, protein and crude fiber in the feedstuff. The total of these percentages subtracted from 100 gives the percentage of nitrogen-free extract, which is

TABLE 16. THE COMPOSITION OF SOME COMMON FEEDSTUFFS

| Feedstuff | Moisture (per cent) | Ash (per cent) | Crude Protein (per cent) | Carbohydrate | | Fat (per cent) |
|---|---|---|---|---|---|---|
| | | | | Crude Fiber (per cent) | N-free Extract (per cent) | |
| Barley | 9.3 | 2.7 | 11.5 | 4.6 | 69.8 | 2.1 |
| Barley shorts | 10.2 | 4.2 | 12.8 | 8.6 | 60.6 | 3.6 |
| Beet pulp, dried | 8.2 | 3.5 | 8.9 | 18.9 | 59.6 | 0.9 |
| Corn | 12.0 | 1.5 | 9.9 | 2.0 | 69.7 | 4.9 |
| Corn cob | 10.0 | 1.5 | 2.0 | 31.8 | 54.3 | 0.4 |
| Corn gluten meal | 9.1 | 1.1 | 35.5 | 2.1 | 47.5 | 4.7 |
| Cottonseed | 9.4 | 4.6 | 19.5 | 22.6 | 24.9 | 19.0 |
| Cottonseed meal | 7.5 | 6.2 | 44.1 | 8.1 | 25.0 | 9.1 |
| Cottonseed hulls | 9.7 | 2.7 | 4.6 | 43.8 | 37.3 | 1.9 |
| Cowpeas | 11.6 | 3.4 | 23.6 | 4.1 | 55.8 | 1.5 |
| Flaxseed | 9.2 | 4.3 | 22.6 | 7.1 | 23.2 | 33.7 |
| Linseed meal | 9.6 | 5.6 | 36.9 | 8.7 | 36.3 | 2.9 |
| Oats | 9.2 | 3.5 | 12.4 | 10.9 | 59.6 | 4.4 |
| Oat hulls | 6.8 | 6.0 | 4.0 | 29.2 | 52.3 | 1.7 |
| Oat kernel | 6.9 | 2.2 | 14.3 | 1.4 | 67.1 | 8.1 |
| Peanut meal | 6.6 | 4.8 | 44.8 | 7.6 | 26.0 | 10.2 |
| Rice bran | 10.1 | 9.7 | 12.1 | 12.4 | 44.3 | 11.4 |
| Rice hulls | 9.3 | 16.9 | 3.3 | 35.4 | 34.0 | 1.1 |
| Sunflower seed cake | 10.0 | 4.2 | 34.8 | 10.9 | 21.8 | 18.3 |
| Wheat | 10.2 | 1.9 | 12.4 | 2.2 | 71.2 | 2.1 |
| Red dog flour | 11.1 | 2.5 | 16.8 | 2.2 | 63.3 | 4.1 |
| Wheat middlings (shorts) | 10.5 | 4.4 | 17.4 | 6.0 | 56.8 | 4.9 |
| Wheat bran | 10.1 | 6.3 | 16.0 | 9.5 | 53.7 | 4.4 |

also included in the proximate analysis. Table 16 gives the chemical composition of some common feedstuffs.

## PREPARATION OF THE SAMPLE FOR ANALYSIS

The various feedstuffs differ so in their nature that it is difficult to give a general method for preparing the sample for analysis. The directions on sampling, previously given on page 15, should be read carefully. In general, the sample should be mixed thoroughly and in such a state of subdivision that the chance removal of any portion will not in the least change the analysis of the remainder. Grinding the sample so that it will pass through a sieve having circular openings 1/25 in. (1 mm.) in diameter is usually sufficient. Thorough mixing is also imperative.

## MOISTURE

The keeping quality and, to some extent, the value of a feedstuff is dependent upon its moisture content. Federal and State laws require that feeds contain not more than a certain maximum percentage of moisture. This maximum percentage is low enough to insure the keeping quality of the feed by preventing enzymatic activity and the growth of yeasts, molds and bacteria. The law, moreover, prevents unscrupulous dealers from increasing the weight of a feed by incorporating into it excessive quantities of water, thereby selling water at feed prices.

Aside from the legal aspect, it is also necessary to analyze feeds for their moisture content so that the percentage of other feed constituents may be reported on a definite moisture basis. This is necessary when comparing the nutritive value of two feeds differing appreciably in their moisture percentages when analyzed. If the analyses are reported on the samples analyzed when air-dried, they are said to be on the air-dry basis. Frequently, analyses on feeds are reported on a 15 per cent moisture basis or on a moisture-free basis.

**Moisture Methods.** The official method for the determination of moisture in feeds requires the drying of a sample of approximately 2 grams in size to a constant weight at 100° C. under a pressure not to exceed 100 mm. of mercury. Alternative methods recognized as official by the A.O.A.C. are: toluene distillation method, drying without heat over a dehydrating agent, and drying a 2 gram sample in an electric oven at 135° C. for exactly 2 hours. Read pages 181–191 for complete discussion of moisture methods.

In making a proximate analysis, the analyst uses the dry sample from the moisture determination for the subsequent crude fat and crude fiber determinations. The toluene distillation method and the 135° C. electric oven drying method do not give the analyst a sample which he can use (drying at 135° C. oxidizes some of the fat). The vacuum oven method gives the proper sample for the crude fat and fiber determinations.

**Moisture Determination by Drying at 100° C. in a Vacuum.** Dry exactly 2.000 gram samples of the well-mixed feed according to the technique described on page 184 for drying at 100° C. in a vacuum. The loss in weight is considered as the weight of moisture present in the sample. Calculate and report the percentage of moisture by drying at 100° C. in a vacuum. Save the dried samples for the ether extract determination.

**Moisture Determination by Drying at 100° C. Without a Vacuum.** Where only comparative moisture values are desired, drying the samples to a constant weight at 100° C. without a vacuum is sufficient. This method also permits the obtaining of dry samples for the crude fat and fiber determinations. Since many laboratories do not have a vacuum oven available, this method will be discussed in detail.

*Procedure.* Weigh exactly 2.000 gram samples of the well-mixed feed into two previously dried and weighed aluminum moisture dishes equipped with tight-fitting covers. Place the covers loosely upon the dishes so that there is ¼ in. opening on one side between the cover and the dish. Place the loosely covered dishes on a shelf in an electrically heated oven regulated to hold constant at 100° C. Do not place the dishes on the oven floor but on the shelves to insure heating at the proper temperature. At the end of a 5-hour heating period, open the door of the oven, immediately tap the covers of the dishes thereby closing them, and remove the dishes to a desiccator to cool. Weigh the dried samples as soon as they have cooled to room temperature (usually 20–30 min. after removal from the oven). Reheat the samples, under the same conditions, for 1-hour periods until a constant weight is obtained or until the sample begins to increase in weight. Calculate and report the loss in weight on drying as percentage of moisture by drying at 100° C. without a vacuum. Save the dried samples for the ether extract determination.

*Remarks.* The sample must not be heated for more than 5 hours at the first heating and not over 1-hour intervals thereafter to prevent fat oxidation. If the sample cannot be dried to constant weight during one laboratory period, store it in the desiccator until the next period. However, whenever a weighing is made, it must follow immediately after the sample is cooled to room temperature and cannot be delayed until the next laboratory period. Dry samples, even in covered dishes, when stored in a desiccator for several days may absorb water from the desiccating agent and then must be redried.

**Moisture Determination by Drying at 135° C. Without a Vacuum.** Weigh exactly 2.000 gram samples of the feed into previously dried and weighed moisture dishes. Cover the dishes loosely as in the drying methods at 100° C., and place the loosely covered dishes in an electric air oven regulated to 135° C. ± 2°. Dry the samples for exactly 2 hours, cover the dishes, cool in a desiccator, and weigh as soon as cool. Calculate the loss in weight on drying as percentage of moisture by drying for 2 hours at 135° C. without a vacuum. This drying method is not recommended if a subsequent crude fat determination is to be made upon the same weighed and dried sample.

## ETHER EXTRACT OR CRUDE FAT

The ether extract or crude fat represents all that material extractable by ether from the sample. Besides the true fat (triglycerides), other materials such as phospholipids, sterols, essential oils, fat-soluble pigments, etc., may be extracted. Water-soluble materials are not extracted since the sample has been thoroughly dried and is extracted with anhydrous ether. With the exception of a few feedstuffs, the percentage of ether extract is usually rather low.

**Determination of Ether Extract by the Continuous Extraction Procedure.** The dry sample is thoroughly extracted with anhydrous ether, the ether evaporated, and the amount of extracted material weighed. Read pages (158–160) for complete discussion on the determination of fat in various products.

*Procedure.* Transfer the dried sample from the moisture determination to a cellulose extraction thimble and plug the top of the thimble with a wad of fat-free cotton. Drop the thimble and contents into a fat extraction tube. The bottom of the extraction tube extends through a stopper by means of which is attached a previously dried and weighed fat-flask. Pour approximately 75 ml. of anhydrous ether through the sample in the tube into the fat-flask. Attach the top of the fat-extraction tube by means of a stopper to one of a bank of condenser tubes especially constructed for fat-extraction work. The fat-extraction flask containing the ether should then be partly submerged in the water bath used to volatilize the ether. The water bath should be regulated so that the ether volatilized will condense and drop continuously upon the sample without any appreciable loss of ether. Continue the extraction of the sample for 16 hours, or longer, to remove all the ether extractable materials.

At the end of the extraction period, remove the flask and extraction tube from the condenser and detach the fat-extraction flask from the extraction tube. Save the thimble containing the extracted sample for the crude fiber determination. Place the fat-flask on the steam bath under a hood and volatilize the ether from the extracted substances. When all the ether has been removed, carefully clean and dry the outside of the flask with a towel. Dry the flask and its contents in a drying oven at 100° C. for 45 min., cool in a desiccator and weigh. Reheat for 30 min., cool and weigh again. Repeat the heating and weighing until a constant weight is obtained or until the flask begins to increase in weight. The weight of ether extract is the increase in weight of the fat-flask and contents over the original weight of the flask. Calculate the percentage of ether extract on both the air-dry and on a 15 per cent moisture basis.

## CRUDE FIBER

A portion of every feed is indigestible as far as the animal is concerned and so only gives bulk to the feed. The greater share of this indigestible matter consists of fiber, associated with varying amounts of other rather indigestible materials. The crude fiber analysis attempts to determine the percentage of this indigestible matter, or roughage, in a feed.

The method employed for the determination of crude fiber attempts to simulate, to some extent, the action taking place upon the feed in the digestive tract of the animal. The feed is first subjected to a dilute acid hydrolysis, then to a dilute alkaline hydrolysis and the residue remaining is considered fiber plus a small quantity of undissolved mineral matter. While the digestion in the animal body is brought about largely by enzymatic action under acid and then more alkaline conditions, most of the digestible matter is also hydrolyzed and converted to a soluble form by heating with dilute acid and alkali. It should be emphasized at this point that the method is strictly empirical, i. e., a certain set of conditions have been established, and must be adhered to, in order to compare the results obtained with those obtained by other investigators. Changing the conditions of the method will result in obtaining quite different amounts of fiber.[1]

The crude fiber content of a feed is a valuable index of the food value of a feed. Crude fiber has practically no food value and its only function in the intestinal tract is to give bulk to the contents and so stimulate intestinal peristaltic action. The State and Federal laws require that a statement of the crude fiber content of the feed be given on the container. This is to prevent unscrupulous dealers from mixing inert waste fibrous materials with feeds and selling these adulterated feeds as pure feeds. All normal feeds, and also foods, have fairly constant fiber contents so that adulteration with a "filler" is rather easily detected.

**Determination of Crude Fiber.** The feed is digested with boiling dilute acid to hydrolyze the carbohydrate and protein materials contained in it. Further digestion with boiling dilute alkali causes the saponification of the fatty material of the feed not extracted by ether. Both treatments contribute to the solution of most of the mineral matter. The residue consisting mainly of fiber and a little mineral matter is filtered off, dried and weighed. It is then ignited to constant weight and again weighed. The difference in the two weights represents the weight of crude fiber present in the sample.

*Reagents and Equipment.*

1. *Sulfuric acid solution.* A solution prepared so that it will contain exactly 1.25 grams of sulfuric acid per 100 ml. of solution.
2. *Sodium hydroxide solution.* A solution prepared so that it will contain exactly 1.25 grams of sodium hydroxide, free from carbonate, per 100 ml. of solution.
3. *Filtering cloth.* Filters are cut from butcher's linen or dress linen cloth with approximately 45 threads to the inch, or the No. 40 filtering cloth made by the National Filter Cloth and Weaving Company, 1717 Dixwell Avenue, Hamden, Conn.

*Procedure.* The dried residue remaining in the extraction thimbles after the extraction of the crude fat is carefully transferred to a 750 ml. Erlenmeyer flask. About 0.5 gram of asbestos is usually added along with the sample. Add 200 ml. of boiling sulfuric acid solution, connect the flask with a reflux condenser and digest the sample at the boiling temperature for 30 min. (The contents of the flask should come to boiling within 1 min. and boil for *exactly*

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[1] Bidwell and Walton, *J. Assoc. Off. Agr. Chem.*, 2, 32 (1916).

30 min.) Rotate the flask at 5-min. intervals to keep the contents of the flask thoroughly mixed. The solid matter has a tendency to stick to the sides of the flask, out of contact with the solution, and this must be avoided as much as possible. A blast of air directed into the flask will help to reduce frothing which may carry the sample up the walls of the flask and even into the condenser at times.[1]

At the completion of the digestion period, filter the contents of the flask through a linen filter supported in a fluted funnel and wash free from acid with boiling water. Bring a quantity of the sodium hydroxide solution to boiling and keep it at this temperature under a reflux condenser until used. As much as possible of the washed residue on the linen filter is transferred back to the Erlenmeyer flask by means of a spatula. The filtering cloth is then spread out in a wide stemmed funnel inserted in the Erlenmeyer flask and the remainder of the residue washed into the flask by means of 200 ml. of the boiling sodium hydroxide solution. A wash bottle marked to deliver 200 ml. of the solution is helpful in effecting this transfer.

Immediately connect the flask to the reflux condenser and boil for 30 min., rotating the flask at 5-min. intervals. At the end of the 30-min. boiling period, remove the flask and filter the contents through the same linen filtering cloth used at the completion of the acid hydrolysis. Wash thoroughly with boiling water and then transfer the contents of the filter, with the aid of a spatula and wash water, to a Gooch crucible prepared with a thin asbestos mat. Wash the Gooch and contents thoroughly with water and then with 15 ml. of ethyl alcohol.

Dry the crucible and contents at 100°–110° C. until a constant weight is attained, cooling the crucible in a desiccator before weighing. Then ignite the crucible and contents in a muffle furnace at a dull red heat (approximately 600° C.) until all organic matter has been destroyed (approximately 20 min.). The loss in weight during incineration represents the weight of crude fiber in the sample. Calculate the percentage of crude fiber present in the feed on the air-dry and also on a 15 per cent moisture basis.

## ASH

The ash content is an indication of the amount of mineral matter present in a feed. The ash, however, does not contain the minerals in the identical combinations present in the feed. The salts of organic acids are usually converted to oxides of the metallic cations through oxidation of the organic acid radical. Some of the phosphorus and sulfur present in strictly organic compounds is oxidized to phosphate and sulfate, respectively, and may combine with cations present in the ash. Some of the phosphorus and sulfur may be volatilized, as may also some of the chloride present, unless special precautions are taken in the ashing process. The ash of feeds is made up principally of the phosphates, chlorides, sulfates, silicates and oxides of calcium, sodium and potassium.

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[1] Gerritz, *Ind. Eng. Chem., Anal. Ed.*, 8, 75 (1936).

**Determination of Ash.** All the organic matter is completely oxidized through incineration and the mineral matter remaining is weighed as ash. Read pages 191–194 for complete discussion on the ash determination.

*Procedure.* Weigh exactly a 2.000 gram sample of the feed into a previously ignited and weighed procelain crucible. Carefully ignite the sample over a Bunsen or Meeker burner under a hood and heat until the sample is thoroughly charred. Transfer the crucible and contents to a muffle furnace held at 600° C. and continue the ashing process until the ash has a gray-white appearance. Cool in a desiccator and weigh. Reheat in the muffle furnace for hour intervals until a constant weight is obtained. From the weight of ash obtained, calculate the percentage of ash in the feed on the air-dry and on a 15 per cent moisture basis.

*Remarks.* Charring the material over a burner is necessary to prevent mechanical loss of ash if the ashing is to be conducted in a hot muffle furnace. Ignition at 600° C. (dull redness) should prevent volatilization of chlorides and also fusion of the ash. If unoxidized material is present when ash fuses, carbonaceous matter may be occluded in the fused ash and too high a result obtained. While the ashing may be completed over a Bunsen or Meeker burner, a muffle furnace is preferable in that the temperature can be controlled more accurately and the possibility of carbon deposition on the crucibles eliminated.

## CRUDE PROTEIN

In general, the most important and most expensive component of a feedstuff is protein. This material is used for tissue building in animals and so must be included in their diet. Proteins are substances made up wholly or largely of amino acids. The distinguishing feature of amino acids is that they contain an amino group ($-NH_2$). The determination of the amount of ammonia ($NH_3$), derived from amino groups, is the basis of the Kjeldahl method of analysis for the amount of protein in a feed.

**Determination of Crude Protein.** The feed is digested with concentrated sulfuric acid in the presence of an oxidizing catalyst until all the organic matter is oxidized and the protein-nitrogen converted to ammonium sulfate. Subsequent addition of strong alkali to the ammonium sulfate liberates the ammonia, which is determined quantitatively by distillation into standard acid. Multiplying the amount of nitrogen found by the factor 6.25, converts the nitrogen to protein. Read pages 151–158 for complete discussion of the protein determination, including the calculations involved.

*Procedure.* Weigh an exactly 1.000 gram sample of the well-mixed feed, wrap it tightly in a filter paper, and drop it into a Kjeldahl flask. Add 15–18 grams of potassium sulfate, 0.3–0.5 gram of copper sulfate, and 30 ml. of concentrated sulfuric acid. Digest, distill, and titrate according to the procedure given on pages 153–157. A "blank" determination involving all the reagents, but not the sample, is made at the same time as the sample determination. Using the general protein factor of 6.25, calculate the percentage of protein present in the feed on the air-dry and on a 15 per cent moisture basis.

## NITROGEN-FREE EXTRACT

The nitrogen-free extract of feeds consists mainly of carbohydrate material, the bulk of which is made up of starch. Since the major constituent of most of the cereal grains is starch, the nitrogen-free extract of feeds from these grains is quite large. Some seeds contain large quantities of protein or oil and, in these instances, the nitrogen-free extract is, of necessity, much smaller. In most feeds then, the nitrogen-free extract represents a great share of the nutritive part of the feed.

Instead of determining the nitrogen-free extract, it is possible to analyze a feed specifically for its content of starch and various soluble sugars, page 180. These determinations, however, are quite difficult and time consuming. Also, since starch and sugars have the same function nutritionally, little is gained by determining them individually. Thus, the general procedure is to determine the nitrogen-free extract on feeds rather than the starch and sugar content.

The nitrogen-free extract is a calculated value rather than the result of a direct laboratory analysis. It is obtained in per cent by subtracting the sum of the percentages of moisture, crude fat, crude fiber, ash, and protein from 100 per cent.

Calculate the percentage of nitrogen-free extract of the feed on the air-dry and also on a 15 per cent moisture basis.

# CHAPTER XII

## MILK

Milk is the natural secretion of the mammary glands of female mammals for the feeding of their young. Milk is considered practically a complete food and, hence, is rather complex in nature. Of the major constituents of milk, the lactose (milk sugar) and some of the mineral salts are in true solution; the milk proteins, of which casein predominates in the form of calcium caseinate, along with lactalbumin and lactoglobulin as well as some of the calcium phosphate exist in colloidal suspension; whereas the fat of milk exists in a macroscopic dispersion in the milk plasma. Besides these constituents, milk also contains carotinoid pigments, whey pigment (lactoflavin), vitamins, and enzymes.

Milks from the different species of mammals differ appreciably in their composition. However, since cows' milk is the milk most commonly used as a food for humans and animals, it will be the only type discussed. Table 17 gives the average composition of cows' milk and milk products.

TABLE 17. AVERAGE COMPOSITION OF COWS' MILK AND MILK PRODUCTS

| Constituent | Fluid Whole Milk (per cent) | Fluid Skim Milk (per cent) | 40 Per Cent Cream (per cent) | Buttermilk (per cent) | Evaporated Whole Milk (per cent) | Dried Whole Milk (per cent) | Dried Skim Milk (per cent) |
|---|---|---|---|---|---|---|---|
| Water | 87.3 | 90.4 | 54.4 | 91.0 | 73.4 | 4.0 | 4.0 |
| Total solids | 12.7 | 9.7 | 45.6 | 9.0 | 26.6 | 96.0 | 96.0 |
| Fat | 3.8 | 0.2 | 40.0 | 0.4 | 8.3 | 26.0 | 1.0 |
| Solids-not-fat | 8.9 | 9.5 | 5.6 | 8.6 | 18.3 | 70.0 | 95.0 |
| Lactose | 4.9 | 5.0 | 3.0 | 4.4 | 10.1 | 36.8 | 49.2 |
| Protein | 3.3 | 3.7 | 2.2 | 3.5 | 6.7 | 27.2 | 37.4 |
| Ash | 0.7 | 0.8 | 0.4 | 0.7 | 1.5 | 6.0 | 8.4 |

Milk from individual cows may differ appreciably from the values given in Table 17 for fluid whole milk due to breed differences, time of year, time of day, fore milk or strippings, etc. These differences are mainly in the relative amounts of fat, protein and water. The percentages of ash and lactose remain practically constant in milk regardless of the other variations. It is for this reason that analytical values dependent on the ash and lactose content of milk are of greatest value in detecting the adulteration of milk.

## FLUID MILK

### PREPARATION OF THE SAMPLE FOR ANALYSIS

Milk fat will rise sufficiently on a milk sample so that its uniformity is destroyed in five minutes. In order, then, to secure a representative sample for analysis, it is necessary to thoroughly mix the milk just before removal of the sample. This is best accomplished by pouring the milk from its container into another vessel and back again several times. If this is not feasible, the milk should be stirred thoroughly. Shaking the milk is to be avoided as this tends to cause a separation of the milk fat.

### SPECIFIC GRAVITY

The specific gravity of milk is influenced by each of its constituents. The solids dissolved or colloidally dispersed in milk tend to raise, whereas the fat particles tend to lower the specific gravity. It might be assumed, then, that the specific gravity would be useful to detect the addition of water to fluid whole milk. Although the specific gravity is lowered upon the addition of water, this may be compensated for by the removal of some of the fat by skimming which raises the specific gravity. So, in itself, specific gravity is of little value for detecting this type of adulteration. Of much greater importance is the use of the specific gravity for the conversion of volumes to weight. This is of especial importance in analytical work since it is much more convenient to measure volumes of milk for analysis than to weigh such samples.

**Determination of Specific Gravity.** The specific gravity of milk may be determined by any of the accepted methods for determining specific gravity (see pp. 113–120). Although the pycnometer method for determining specific gravity is the more accurate, it is also more time consuming, so that the specific gravity of milk is usually determined by either the Westphal balance or hydrometer methods.

A special hydrometer covering the range of specific gravities ordinarily met with in milk is called a lactometer. The Quevenne lactometer has a scale graduated into degrees from 15 to 40, corresponding to specific gravities from 1.015 to 1.040. Readings on this lactometer then may be converted easily to specific gravities by prefixing 1.0 to the degrees read. The New York Board of Health lactometer is graduated into arbitrary degrees in such a manner that 0° corresponds to a specific gravity of 1.000, and 100° to a specific gravity of 1.029, the latter figure being considered as the average specific gravity of milk. Degrees on this lactometer thus would indicate roughly the percentage of whole milk in a milk-water mixture.

Hydrometers must be used at the temperature for which they are calibrated or the reading must be corrected. The Quevenne lactometer is calibrated for 60° F. so that readings taken with it at temperatures other than that are corrected to 60° F. by adding or subtracting 0.1 lactometer degree for each degree F. above or below 60° F. It is always advisable to obtain the specific gravity reading near 60° F. (15.55° C.).

## TOTAL SOLIDS

Instead of determining the percentage of moisture it is customary, in the case of fluid whole milk, to determine the percentage of dry matter or total solids. Subtracting the percentage of total solids from 100 will, of course, give the percentage of water present in the sample. Although the percentage of total solids is fairly constant for market milk, it may vary appreciably for individual samples from cows.

**Determination of Total Solids by Drying.** A measured quantity of milk is transferred into a weighed flat dish containing a layer of sand or asbestos. The dish and contents are dried to constant weight at 100° C. and the increase in weight of the dish due to the total solids is determined. The sand or asbestos greatly increases the drying surface and so aids in preventing film formation that would cause a decreased rate of evaporation at the elevated temperature.

*Procedure.* To a flat aluminum or porcelain dish, 6–10 cm. in diameter, add 10–15 grams of white sand. The dish and sand are heated at 100° C. in a drying oven until a constant weight is obtained. Then add 1.5–3 ml. of the well-mixed milk sample to the dish and weigh quickly. Dry on the steam bath for 30 min. and then at 100° C. in a drying oven (preferably vacuum) until constant weight is obtained. Cool in a desiccator before weighing and weigh as rapidly as possible. From the amount of total solids determined in this way and the weight of the sample analyzed, calculate the percentage of total solids present.

*Remarks.* The dried solids in the dish should be practically white. If any appreciable browning has occurred, it is an indication that some of the lactose has been caramelized and that the results will be somewhat in error.

**Determination of Total Solids from the Lactometer Reading and the Percentage Fat.** Instead of actually determining the percentage of total solids, the value may be approximated very closely, if the specific gravity and fat percentage of the milk are known. The calculation is based upon the fact that the constituents of a normal milk are present in a fairly constant ratio. If this is true, then having determined two of the factors involved, the third can be calculated with a fair degree of accuracy. One of the simplest formulas for this calculation was proposed by Hehner and Richmond in 1888, as follows:

$$\text{T.S.} = \frac{\text{L}}{4} + 1.2f + 0.14$$

where *T.S.* is the percentage of total solids; *L*, the Quevenne lactometer reading; and *f*, the percentage of fat. For example, with a lactometer reading of 32.0 (specific gravity 1.032) and a fat content of 4.00 per cent, the percentage of total solids in the milk would be:

$$\frac{32}{4} + 1.2 \times 4 + 0.14 = 12.9 \text{ per cent.}$$

## ASH

The ash content of milk does not give a true picture of the mineral matter as it exists in the fluid milk. In the ashing process, the organic radicals of a number of the salts are oxidized and lost, leaving the metallic elements as oxides. Furthermore, some of the sulfur and phosphorus present in strictly organic compounds are oxidized and find their way into the ash.

The mineral content of normal milk is fairly constant even for samples from individual cows. This is true because milk is isotonic with blood and so, of necessity, its mineral matter will vary within narrow limits. Because of this fact, the freezing point of milk which is dependent upon the amount of dissolved substances, and especially upon the highly dissociated minerals in solution, is also fairly constant. The addition of water to milk reduces the concentration of mineral salts and proportionately raises the freezing point. This relationship makes possible the ready detection of more than 3 per cent of added water to fluid milk. The method usually used to detect added water in this way is known as the Hortvet Cryoscopic Method.[1]

**Determination of Ash.** The organic matter in a weighed sample of milk is oxidized by heating with the aid of nitric acid. The remaining inorganic residue of mineral matter, or ash, is weighed and the percentage of ash calculated. Read pages 191–194 for a general discussion on ashing methods.

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[1] Assoc. Off. Agr. Chem., "Methods of Analysis," 5th Ed., 1940, p. 275.

*Procedure.* Heat a porcelain dish of approximately 50 ml. capacity at a temperature just below redness (550° C.) for 1 hour, cool in a desiccator and weigh. Pipette about 20 ml. of the milk sample into the dish and weigh as quickly as possible. Add 6 ml. of concentrated nitric acid and evaporate to dryness on the steam bath. Transfer the dish and dried sample to a muffle furnace held at 550° C. and heat until the ash is free from carbon (ash is white). Cool in a desiccator, weigh, and report the increase in weight of the dish as ash. From this result and the weight of the sample analyzed, calculate the percentage of ash.

*Remarks.* The milk sample is evaporated on the steam bath to eliminate the bulk of the water present. Nitric acid facilitates the oxidation of the organic matter and is, itself, entirely volatilized at the completion of the ashing process. Since milk contains appreciable quantities of sodium and potassium chlorides, and since chlorides would be volatilized at high temperatures, the ashing temperature is kept at 550° C. or less. The muffle furnace permits a much more accurate control of the ashing temperature and consequently is preferable to ashing over a gas flame.

## FAT

The fat content of milk tends to vary more than any of the other milk constituents. Certain of the dairy breeds are noted for their ability to produce milk rich in fat. The public has always attached more importance to the fat content or "richness" of milk than to any of the other constituents. This has led to the purchase and sale of milk on the basis of its fat content. Most states have laws regulating the minimum fat content permitted in the milk sold in those states. These facts indicate the importance of the fat determination in milk.

Various methods for the determination of the fat content of milk have been developed. The most important types of methods are the Babcock method and the Röse-Gottlieb or Mojonnier methods. Read pages 158–160 for the general discussion on the fat determination in agricultural and biological products.

**Determination of Fat by the Babcock Method.** The Babcock method is a rapid method for general dairy control testing. The test depends upon the fact that, when milk is treated with concentrated sulfuric acid, the proteins of the milk are first precipitated and then dissolved, permitting the fat to rise in a layer at the top. The fat layer is measured in a calibrated tube and, from this value, the percentage of fat present may be calculated.

*Reagent and Apparatus.*

1. *Concentrated sulfuric acid* with a specific gravity of 1.82–1.83 at 20° C.
2. *Centrifuge* capable of being electrically or otherwise heated to 55°–60° C. The proper speed of the centrifuge will depend upon the size of the wheel. The following r.p.m.'s should be used for the corresponding wheel diameters: 10 in.–1074; 12 in.–980; 14 in.–909; 16 in.–848; 18 in.–800; 20 in.–759; 22 in.–724; and 24 in.-693.
3. *Divider or calipers* for measuring the height of the fat column.
4. *Graduated cylinder or pipette* graduated to deliver 17.5 ml. of the sulfuric acid.
5. *Standard Babcock test milk bottle* approximately 6 in. in height, with a neck not less than 63.5 mm. long graduated from 0 to 8 in unit per cents, and intermediate graduations between the units representing tenths of a per cent (Fig. 42).
6. *Standard milk pipette* graduated to contain 17.6 ml. of water at 20° C., with a delivery time of 5–8 seconds, and a maximum error in graduation not to exceed 0.05 ml. Check the pipette by measuring from a burette the volume of water at 20° C. which it holds up to the graduation mark.
7. *Water bath* held at 55°–60° C.

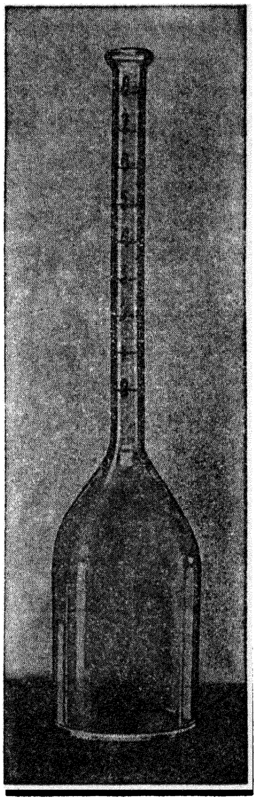

FIG. 42. Babcock Milk Flask. (From Jacobs' "Chemical Analysis of Foods and Food Products," D. Van Nostrand Co., Inc.)

*Procedure.* Secure, with the aid of the milk pipette, a 17.6 ml. sample of the well-mixed milk. Transfer the sample to the standard test milk bottle, blowing out the milk in the tip after it has ceased flowing. Hold the test bottle at an angle and pour the sulfuric acid (temperature 15°–20° C.) into it slowly, in small portions, while rotating the bottle to wash all milk into the bulb of the bottle. Thoroughly mix the acid and milk with a rotary motion (so that no liquid gets into the neck of the bottle) until all traces of curd have disappeared. When the acid and milk are properly mixed, the mixture becomes hot and turns uniformly dark colored.

Transfer the bottle to a centrifuge and counterbalance with another sample bottle or bottle containing water. When the centrifuge has attained the proper speed (depending upon the diameter of the wheel), whirl the sample for 5 min. Remove the bottle and add hot distilled water (60° C. or more) until the bulb of the bottle is filled. Centrifuge for 2 min. at the proper speed. Again add hot water until the fat column is forced into the neck of the bottle, and the liquid approaches the top graduation on the bottle. Centrifuge 1 min. at 55°–60° C.

Place the bottle into the water bath held at 55°–60° C., immersing it to the level of the top of the fat column. When equilibrium is attained, as evidenced by no change in the lower fat surface, remove the bottle from the bath, dry, and measure the height of the fat column with dividers or calipers. The fat column is measured from its lower surface to the highest point of the upper meniscus and is read directly in per cent by weight of fat in the milk.

*Remarks.* When measured, the fat column should be translucent golden yellow in color and be free from visible suspended particles. Should the fat be light colored and frequently have white particles beneath it, there is indication that the acid was too weak, the milk too cold when the acid was used, or insufficient acid was used. Should the fat be dark colored and contain dark specks, it is an indication that too much acid or too strong an acid was used.

**Determination of Fat by the Röse-Gottlieb Method.** The Röse-Gottlieb method is based on somewhat the same principle as the Babcock test, i. e., it is a wet extraction method. However, it is the more accurate method of the two. The Röse-Gottlieb method is the basis of the Mojonnier method which is one of the most widely used methods for determining the fat content of dairy products including fluid whole milk, skim milk, buttermilk, cream, powdered milks, and ice cream.

The fat, freed from the other milk constituents by treatment with alcohol and ammonia, is dissolved in a mixture of equal parts of petroleum and ethyl ether. The ether layer, containing the fat, is removed to a dish, the ethers evaporated and the fat weighed.

*Procedure.* Transfer a weighed sample of approximately 10 grams of the well-mixed milk (readily weighed with the aid of a Mojonnier weighing pipette and holder) to a Röhrig tube or similar apparatus (Figs. 43 and 44), add 1.3 ml. of concentrated ammonium hydroxide solution and mix thoroughly. Add, in the order given, the following reagents, shaking for 30 sec. after the addition of each reagent: 10 ml. of 95 per cent ethyl alcohol, then 25 ml. of ethyl ether, and then 25 ml. of petroleum ether. Allow the mixture to stand until the ether layer is practically clear (about 20 min. is usually sufficient). Carefully siphon off as much as possible of the ether layer into a dish or fat-flask. Re-extract the liquid remaining, twice with 15 ml. portions of each of the ethers, and add these ether extracts to that previously obtained. Evaporate the ethers on a steam bath and dry the dish and fat in a drying oven at 100° C. for 45-min. periods to constant weight. Dissolve and completely remove the fat in the dish with petroleum ether, retaining any non-fat residue which may have come over in the extraction. Again dry the dish and any residue, if present, to constant weight. The difference between these two weights will be the weight of fat in the sample. Calculate the per cent of fat in the sample.

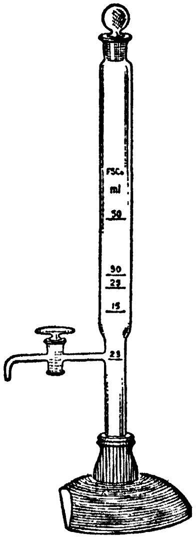

FIG. 43. Rohrig-Biesterfield Milk Fat Extraction Tube. (Courtesy of Fisher Scientific Co.)

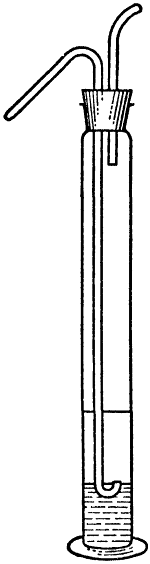

FIG. 44. Milk Fat Extraction Tube which may be Used in Place of the Rohrig Tube.

**Determination of Fat by the Mojonnier Method.** This method is almost identical with the Röse-Gottlieb except that a different type of extraction flask is used, necessitating the decanting of the ether-fat layer instead of siphoning it off from the aqueous solution. Also, the extracted fat is dried for a shorter period of time at a higher temperature.

*Procedure.* Transfer 10 grams of the well-mixed milk, with the aid of a Mojonnier weighing pipette and holder, into a Mojonnier flask (Fig. 45), add 1.5 ml. of concentrated ammonium hydroxide solution and mix thoroughly in the small bulb of the flask. Add 10 ml. of 95 per cent ethyl alcohol, cork the flask, and, holding it horizontally with a finger on the cork, shake thoroughly. Add 25 ml. of ethyl ether and shake as before for 30 sec., then add 25 ml. of petroleum ether and again shake for 30 sec. Place the flask in a vertical position in a beaker, box, or stand for 5 min.

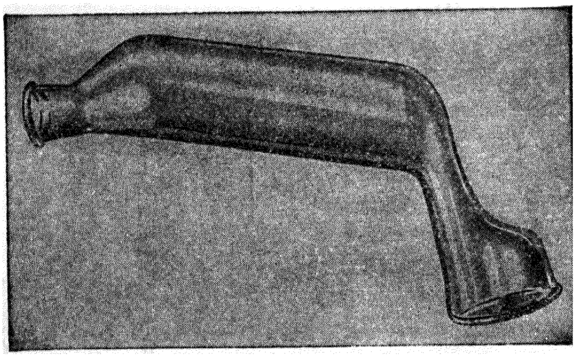

FIG. 45. Majonnier Extraction Tube. (From Jacobs' "Chemical Analysis of Foods and Food Products," D. Van Nostrand Co., Inc.)

Remove the cork and carefully decant off as much as possible of the ether layer into a weighed aluminum dish. By holding the flask in a horizontal position with the small bulb down, a fine separation of the layers may be made, especially if the dividing line is at the upper level of the constriction between the small and the large bulb.

Re-extract, in the same manner, the remaining liquid by adding, successively, 5 ml. of ethyl alcohol, 15 ml. of ethyl ether, and 15 ml. of petroleum ether, shaking thoroughly after each addition. Let stand for 5 min. and if the dividing line is not at the upper level of the constriction, add water to bring it to that point. Decant off the ether layer into the dish containing the first ether extraction. Evaporate off the ethers on the steam bath and dry in a drying oven at 135° C. for 5 min. Cool in a desiccator and weigh. Calculate the percentage of fat present in the sample from the weight of fat obtained.

## ACIDITY

The acidity of milk is due to acid phosphates and to lactic acid. Bacteria present in milk ferment the lactose to lactic acid. When sufficient lactic acid is produced, the proteins coagulate and the milk is said to be "sour."

**Determination of the Acidity.** A measured volume of milk of known specific gravity is titrated with a solution of standard alkali and the amount of acid found calculated as percentage of lactic acid.

*Procedure.* A 20.0 ml. volume of the well-mixed milk sample of known specific gravity is accurately measured into a porcelain casserole or cup. Phenolphthalein indicator is added and the milk is titrated with standard 0.1 N alkali solution until a pink color appears and remains for 1 min. From the titration value obtained and the known specific gravity of the milk, calculate the acidity as percentage of lactic acid (1 ml. of 1.0 N alkali solution is equivalent to 1 ml. of 1.0 N lactic acid which will contain 0.090 grams of lactic acid).

## PROTEIN

The principal protein of milk is casein, present in the milk to the extent of about 3 per cent. The next most important protein, lactalbumin, is present in milk to the extent of about 0.5 per cent, whereas lactoglobulin is present only in about 0.05 per cent. The two proteins, casein and lactalbumin, which constitute the major portion of the proteins of milk, contain approximately 15.7 per cent of nitrogen. Thus the factor for converting nitrogen to protein in milk is 100/15.7 or 6.38, rather than the conventional 6.25 as used in feeds. The Kjeldahl method is normally used for determining the total protein content of milk.

**Determination of Total Protein.** All organic matter is oxidized by wet oxidation with sulfuric acid and the protein-nitrogen converted to ammonium sulfate. Subsequent addition of strong alkali to the ammonium sulfate solution liberates the ammonia, which is determined quantitatively by distillation into standard acid. Multiplying the amount of nitrogen found by 6.38 will give the amount of protein present. Read pages 151–158 for complete discussion on the protein-nitrogen determination.

*Procedure.* The general protein procedure (p. 153) is applicable to milk with minor modifications. Transfer, with the aid of a Mojonnier weighing pipette and holder, a weighed sample of approximately 5 grams of the well-mixed milk into the bottom of an 800 ml. Kjeldahl flask. Add the various reagents (15–18 grams of potassium sulfate, 0.3–0.5 gram of copper sulfate, and 25 ml. of concentrated sulfuric acid). Digest and distill as previously described on pp. 153–7 except that 25.00 ml. of 0.1 N standard acid in the receiving flask is sufficient to collect all the ammonia distilled. Conduct a blank determination along with the samples. From the titration values on the samples and the blank, calculate the percentage protein present in the milk, using the factor 6.38 for the conversion of nitrogen to protein.

## MILK SUGAR—LACTOSE

The carbohydrate content of milk consists essentially of lactose. This is a disaccharide giving upon hydrolysis glucose and galactose. Lactose is approximately one sixth as sweet as sucrose and is not fermented by yeast. This latter property is utilized in analyzing certain foods and feeds for their milk content by fermenting away all other carbohydrates present with yeast and determining the lactose which remains.[1] Since the lactose content of milk is fairly constant, a fair approximation of the milk content can be made from the amount of lactose found.

Lactose exhibits reducing properties and readily reduces the copper in Fehling's solution to cuprous oxide. This property is the basis for several analytical methods for the determination of lactose. Lactose solutions also exhibit optical activity and this affords the basis of still another analytical method for its quantitative determination.

**Determination of Lactose by the Munson-Walker Method.** To a weighed portion of milk is added a protein precipitating agent. The precipitated protein and adsorbed fat is filtered off, leaving the lactose and salts in solution. An aliquot of the lactose solution heated with an alkaline copper sulfate solution causes the reduction of copper to cuprous oxide. The amount of cuprous oxide formed is proportional to the amount of lactose present under the conditions of the experiment, consequently the amount of lactose may be read from a table. Read pages 160–180 for complete discussion on copper reduction sugar methods.

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[1] Magraw and Copeland, *Cereal Chem.*, **13**, 541 (1936); Magraw, *J. Assoc. Off. Agr. Chem.*, **23**, 640 (1940).

*Reagents.* See page 164 for the preparation of the various reagents required in the method.

*Preparation of the Sample for Analysis.* Transfer 25 grams of the well-mixed milk sample into a 500 ml. volumetric flask. Add 350–400 ml. of water, exactly 10 ml. of Fehling's copper sulfate solution, and 44 ml. of 0.1 N sodium hydroxide solution or its equivalent. The solution should have an acid reaction and contain copper in solution. Exact measurement of the copper sulfate and sodium hydroxide solutions is absolutely necessary in order to secure a solution which will filter rapidly and give a clear filtrate. The colloidal cupric hydroxide forms a flocculent precipitate which carries down with it the fat and proteins, thereby clarifying the solution. Dilute to the 500 ml. mark with water, shake thoroughly, and filter through a dry filter. Lactose is determined in an aliquot of the filtrate.

*Procedure.* Regulate a burner so that it will cause a 400 ml. beaker, covered with a watch glass and containing 25 ml. of each of the two Fehling's solutions plus 50 ml. of water, to come to a boiling temperature in exactly 4 min. Pipette accurately a 50.0 ml. aliquot of the above prepared lactose-containing filtrate into a 400 ml. beaker and add 25 ml. of each of the two Fehling's solutions (the copper sulfate and the alkaline tartrate solutions). Immediately cover the beaker with a watch glass and bring to a boil in 4 min. over the previously regulated burner. Boil for *exactly* 2 min., and filter *immediately* through a previously prepared, dried, and weighed Gooch crucible using suction. Wash the curpous oxide precipitate thoroughly with 300 ml. of hot water. Empty the hot water out of the suction flask and continue washing the crucible first with 10 ml. of 95 per cent ethyl alcohol and then with 10 ml. of ethyl ether, using suction. Dry the crucible and precipitate for 45 min. at 100° C. in a thermostatically controlled drying oven, cool for 20 min. in a desiccator, and weigh. Reheat for a 30-min. period, cool and reweigh. Continue the reheating and weighing until a constant weight is attained. Obtain the weight of lactose corresponding to the weight of cuprous oxide found in the Munson and Walker table (p. 165). Calculate the percentage of lactose present in the sample from the weight of lactose found in the aliquot of the sample.

**Saccharimetric Determination of Lactose.** A measured volume of milk of known specific gravity, or a weighed portion of milk, equal in weight to twice the normal weight of lactose, is treated with a clarifying agent, diluted to definite volume, and the percentage lactose determined on the filtrate by means of a saccharimeter. An error in volume is introduced due to the volume of the precipitate formed by the clarifying agent and this error is corrected for, either by adding a volume of water equal to the volume of the precipitate, or by determining the effect of the error on the saccharimeter reading and correcting for it.

*Reagents.*

1. *Acid mercuric nitrate solution* prepared by dissolving mercury in twice its weight of nitric acid and diluting this volume with five equal volumes of water.
2. *Phosphotungstic acid solution* prepared by dissolving 5 grams of phosphotungstic acid in 95 ml. of water.

*Procedure for the Single Dilution Method.* Obtain the specific gravity of the milk sample. The volume of sample to be used for the determination will vary with the specific gravity. This volume must be measured at the same temperature at which the specific gravity was taken. The correct volume will be found in Table 18.

TABLE 18. VOLUMES OF MILK CORRESPONDING TO DOUBLE THE NORMAL WEIGHT OF LACTOSE

| Specific Gravity of Milk | Volume of Milk for Double the Normal Weight of Lactose (Ventzke Scale) | Specific Gravity of Milk | Volume of Milk for Double the Normal Weight of Lactose (Ventzke Scale) |
|---|---|---|---|
| 1.024 | 64.25 | 1.031 | 63.80 |
| 1.025 | 64.20 | 1.032 | 63.75 |
| 1.026 | 64.15 | 1.033 | 63.70 |
| 1.027 | 64.05 | 1.034 | 63.65 |
| 1.028 | 64.00 | 1.035 | 63.55 |
| 1.029 | 63.95 | 1.036 | 63.50 |
| 1.030 | 63.90 | | |

This amount of sample is based upon twice the normal weight of lactose (normal weight 32.9 grams per 100 ml. solution) for the Ventzke sugar scale.

Transfer the volume of sample indicated in Table 18 into a 102.6 ml. volumetric flask and add 20 ml. of the acid mercuric nitrate solution. Bring to the mark with 5 per cent phosphotungstic acid solution. Let stand for 15 min. or longer with frequent shaking. Filter the mixture through a dry filter, discarding the first 10 ml. of filtrate. Collect the filtrate and fill a 400 mm. saccharimeter tube. Place the tube in the saccharimeter and obtain the reading on the A scale with the K scale set at zero (read pages 129–132 on the use of the saccharimeter). The reading obtained must be corrected since the sample was twice the normal weight and was viewed in a tube twice the length specified for reading directly. The observed reading is then 2 × 2 too great and must be divided by 4 to give the percentage of lactose present in the sample.

*Remarks.* In this method it is assumed that the average volume of the precipitate obtained by treating a weight of milk equivalent to twice the normal weight of lactose with a clarifying agent is 2.6 ml. Diluting the sample to 102.6 ml., then, should compensate for the volume of the precipitate and the lactose should be contained in 100 ml. of solution. However, the assumption that this precipitate will have a volume of 2.6 ml. is not exactly valid. Considerable deviation from this average has been found for individual samples of milk and an appreciable error may be introduced. The more accurate procedure is the double dilution method, which determines and corrects for the actual volume of precipitate in the particular milk sample being analyzed.

*Procedure for the Double Dilution Method.* Transfer accurately weighed samples of the well-mixed milk, each equal to twice the normal weight of lactose, into a 100 ml. and into a 200 ml. volumetric flask. Add to each flask, 20 ml. of the acid mercuric nitrate solution. To the 200 ml. flask add 15 ml. of the 5 per cent phosphotungstic acid solution and dilute to the mark with water. Dilute the contents of the 100 ml. flask to the mark with the 5 per cent phosphotungstic acid solution. For a period of 15 min. shake both flasks frequently, then filter each through a dry filter, place each solution in a 400 mm. saccharimeter tube and determine their readings in a saccharimeter. Because of the low concentration of lactose in the sample, 400 mm. saccharimeter tubes are used in preference to 200 mm. tubes.

*Calculation of Percentage Lactose Using the Double Dilution Method.* The readings obtained for each solution are in error due to the volume of the precipitate formed by the clarifying agent. Since both solutions contained the same quantity of milk, they both should give the same volume of precipitate. However, the effect of the precipitate error will be twice as great in the 100 ml. solution as in the 200 ml. solution. In this way, half of the effect of the precipitate error may be obtained from the saccharimeter readings on the 100 and the 200 ml. solutions. The total effect may then be calculated and applied as a correction to the readings.

For example, suppose the readings obtained on a milk sample by following the above directions for the saccharimetric method for lactose were 20.2 for the 100 ml. solution and 9.85 for the 200 ml. solution. If no error was introduced by the precipitate, the reading on the 200 ml. solution should be exactly one half that of the 100 ml. solution. On multiplying the reading for the 200 ml. solution by 2, a value is obtained which is less than the reading on the 100 ml. solution. This difference obtained represents one half the error of the precipitate.

$9.85 \times 2 = 19.70$ (twice the reading on the 200 ml. solution).
$20.20 - 19.70 = 0.50$ (one half the precipitate error).
$0.50 \times 2 = 1.00$ (total precipitate error).
$20.20 - 1.00 = 19.20$ (corrected reading on the 100 ml. solution).

The reading obtained by these calculations must be corrected further since the sample was twice the normal weight and was viewed in a tube twice the length specified for reading directly. The reading is then 2 × 2 too great and must be divided by 4 to give the correct percentage of lactose in the sample.

$19.20 \div 4 = 4.80$ (percentage of lactose in the sample).

**Determination of Lactose by the Folin-Wu Colorimetric Method.** A clarified sample of the milk is heated with an alkaline copper solution in a special tube to prevent reoxidation The cuprous oxide obtained is treated with phosphomolybdic acid solution which produces a blue color. The intensity of color is compared in a colorimeter with that of the colored solution obtained by treating a sugar solution of known concentration in the same manner as the sample.

*Reagents.*

1. *10 per cent sodium tungstate solution.* Dissolve 10 grams of sodium tungstate in 90 grams of water.
2. *Standard lactose solution.* Dissolve exactly 0.6000 gram of pure lactose monohydrate in water and dilute to a liter.
3. *Alkaline copper reagent.* Place 40 grams of pure anhydrous sodium carbonate in a liter volumetric flask and dissolve it in 400 ml. of water. Dissolve in this solution, first 7.5 grams of tartaric acid, and then 4.5 grams of crystalline copper sulfate. Dilute to volume and mix thoroughly. If a sediment of cuprous oxide forms upon standing a week or two, siphon off the supernatant liquid or filter through a good grade of filter paper.

4. *Phosphomolybdic acid solution.* Place 35 grams of molybdic acid, 5 grams of sodium tungstate, 200 ml. of 10 per cent sodium hydroxide solution, and 200 ml. of water in a beaker. Boil vigorously for 20–40 min. to remove practically all the ammonia present in the molybdic acid. Cool and transfer to a 500 ml. volumetric flask using sufficient water to bring the volume to about 350 ml. Add 125 ml. of concentrated phosphoric acid (85 per cent) and dilute to volume with water.
5. *Sulfuric acid solution, 2/3 N.* Prepare from a 1 N solution by dilution.

*Procedure.* Pipette accurately 1.00 ml. of milk into a 100 ml. volumetric flask, add 2.0 ml. of the 10 per cent sodium tungstate solution, and then, drop by drop, 2.0 ml. of 2/3 N sulfuric acid solution. Mix thoroughly and allow to stand 5 min. Dilute to volume with water, mix thoroughly, and filter, discarding the first 5–10 ml. of filtrate.

Pipette accurately 1.00 ml. of the filtrate and 1.0 ml. of water into a Folin-Wu sugar tube. Pipette into a similar tube, exactly 2.00 ml. of the standard lactose solution. Add 2.0 ml. of the Folin-Wu alkaline copper reagent to each tube and place the tubes in a beaker of boiling water for 8 min. Cool and add 4.0 ml. of the Folin-Wu phosphomolybdic acid solution. Let stand for 1 min., then dilute to the 25 ml. mark with a 1:4 dilution of the phosphomolybdic acid solution.

Mix thoroughly and compare the two colored solutions in a colorimeter. The intensity of the colored solutions is directly proportional to the amount of lactose present. With this information and the help of Beer's law, calculate the milligrams of lactose in 1.0 ml. of the milk sample. If the specific gravity of the milk is known, calculate the percentage lactose in the milk.

## DRIED MILK

Dried milk is produced either by spraying a fine mist of liquid milk into a heated chamber (spray dried) or by drying a thin film of the liquid milk on a hot roll (roller dried). A product containing approximately 4 per cent water results. Greater moisture content than this is conducive to spoilage by microorganisms, whereas a very low moisture content is conducive to fat oxidation. In addition to liquid whole milk, the following milk products are dried: skim milk, buttermilk, whey, and cream.

Dried milk is widely used in various foods and feeds. This has necessitated the development of methods for the analysis of dried milk itself and also of numerous products for their dried milk content. Most of the analytical methods for liquid whole milk are applicable to dried milk with minor modifications. However, the determination of the milk solids content of products such as bread or feeds is not so readily accomplished. Dried milk is very hygroscopic, consequently samples must be weighed rapidly.

### ANALYSIS OF DRIED MILK

**Determination of Moisture by the Toluene Distillation Method.** Although moisture in dried milks may be obtained by drying to constant weight at 100° C. in a vacuum, the toluene distillation method is more generally used since the high sugar content of dried milk causes some difficulty when drying at elevated temperatures. Read pages 186–188 for complete discussion of the moisture determination by distillation methods.

*Procedure.* Place sufficient dry sand in a 300 ml. Erlenmeyer flask to cover the bottom of the flask and add 75–100 ml. of toluene. Introduce 25.0 grams of the dried milk into the flask and set up the apparatus as illustrated on page 187, using the modified apparatus (Fig. 41). Pour toluene through the top of the condenser until the collecting tube is filled. Conduct the distillation as described on page 186. When the distillation is complete, remove the flame, disconnect the collecting tube and centrifuge it. After allowing the collecting tube to set until it attains room temperature, read the volume of water distilled and, assuming its specific gravity to be 1.00, calculate the percentage of water present in the sample.

**Determination of Total Protein by the Kjeldahl Method.** Weigh, accurately and quickly, a 1 gram sample of the dried milk, wrap it tightly in a filter paper, and drop into a Kjeldahl digestion flask. Add the proper reagents, digest, and distill as in the protein determination of liquid milk, page 213. Multiply the percentage of nitrogen by the factor 6.38 to convert to percentage of protein.

**Determination of Ash.** Weigh, accurately and quickly, a sample of approximately 1 gram into a porcelain or platinum crucible. Carefully char over a burner at a low heat and ignite to constant weight at 550° C. in a muffle furnace. Calculate the percentage of ash.

**Determination of Fat by the Röse-Gottlieb Method.** This method is identical with that for liquid milk except that the dried milk must be put into solution before it can be extracted.

*Preparation of the Milk Solution.* Weigh, accurately and quickly, a sample of approximately 1 gram of the dried milk into a

Röhrig tube or Mojonnier fat extraction flask. Add 10 ml. of water and shake until a homogeneous suspension is obtained, warming if necessary. Add 1 ml. of ammonium hydroxide solution, heat in a water bath at 60°–70° C. for 15 min. with occasional shaking and then cool.

*Procedure.* Add 10 ml. of ethyl alcohol to the milk solution and shake. Extract as in the procedure given for liquid whole milk (pp. 210–13).

**Determination of Lactose Saccharimetrically, Using the Double Dilution Method.** Weigh, accurately and quickly, two 8.225 gram samples; transfer the one to a 100 ml. and the other to a 200 ml. volumetric flask. Add 50–60 ml. of water and shake until a homogeneous solution is obtained. Add to each flask 20 ml. of the acid mercuric nitrate solution (p. 216), shake, and continue from this point as in the procedure for liquid whole milk on page 217.

The correction for the precipitate is made as in the procedure for liquid whole milk. However, since a sample weight equivalent to one fourth the normal weight of lactose was used, the reading must be multiplied by 4 to get it on the basis of a normal weight. If a 400 mm. saccharimeter tube was used, the reading is twice as great as it should be. The net result under these conditions would be to multiply the reading obtained on the 100 ml. solution, corrected for precipitate error, by 2, to obtain the percentage of lactose.

# CHAPTER XIII

# BUTTER

The standard of identity for butter established by Act of Congress, approved March 4, 1923 states: "Butter is the food product which is made exclusively from milk or cream, or both, with or without common salt, and with or without additional coloring matter. It contains not less than 80 per cent by weight of milk fat, all tolerances having been allowed for."

## ANALYSIS OF BUTTER

Butter is analyzed to determine if it will meet the standards established by law as stated above. Perhaps the most common violation of the standard established is either knowingly or unknowingly incorporating excessive quantities of water in butter with a corresponding decrease in the fat content. Such butter may be reworked and the excessive water removed.

The substitution of a cheaper foreign fat for butter fat was a type of violation quite common in that period previous to and during the development of the Food Laws. At present, this violation has been practically eliminated due to the ease with which it is detected.

**Preparation of the Sample for Analysis.** A representative sample of butter secured from a churn, tub, or package is placed in a dry stoppered flask of approximately 500 ml. capacity. The sample is warmed to a creamy consistency in a water bath at 38°–43° C., with stirring at frequent intervals. Except when the sample is being stirred, the flask should be kept tightly stoppered to prevent any loss in moisture. Care must also be taken in the warming process that the fat does not melt and oil off, thereby disrupting the physical structure of the butter. If the sample becomes too fluid in consistency, it may be cooled by holding the flask under the cold-water tap with constant shaking until the desired consistency is attained. The weighed samples for the individual analyses should be removed as quickly as possible from the thoroughly mixed sample before it solidifies and squeezes out water droplets, destroying the homogeneity of the sample.

**Analysis of Butter for Percentage of Moisture, Fat, and Sodium Chloride by the Modified Kohman Method.**[1] Clean, dry, and weigh two aluminum cups of 250 ml. capacity, each equipped with a watch glass. Transfer approximately 10 grams of the well-mixed butter sample into each of the aluminum cups and immediately cover with the watch glasses. Weigh immediately to determine the exact weight of each sample.

*Determination of Moisture.* Remove the watch glasses, place the cups on an asbestos covered gauze and carefully heat over a low flame. Continue the heating until the fat attains a golden-brown color and no appreciable amount of bubbles due to water are given off. It is advisable to shake the cup and contents several times throughout the heating period to break up the casein coagulum causing its complete dehydration and coagulation into a solid which settles out in a grainy condition. A temperature of 135°–145° C. is ideal and a hot plate, if available, may be used to advantage in place of a free flame. At the completion of the heating period the cup and contents are cooled to room temperature in the open, the correct watch glass added, and then a weight obtained. The loss in weight from the original is the weight of moisture. Calculate the per cent of moisture present in the sample.

*Determination of Fat.* Place 150 ml. of petroleum ether in the cup, stir thoroughly, and then allow to stand 3 min. In this way the fat is dissolved in the ether and, after standing for the allotted time, the salt and curd should settle to the bottom. Carefully decant off the supernatant ether into a waste ether bottle. Add another portion of 150 ml. of petroleum ether to the cup and contents. Again stir thoroughly and allow to stand for 3 min. to permit the salt and curd to settle out. Decant the supernatant ether into the waste ether bottle. Drive off the ether remaining in the cup by placing on the steam bath or over a radiator. Then dry the cup and contents on an asbestos pad over a free flame, or on a hot plate. When dry, the contents of the cup should be in the form of a dry powder. Cool in the open, cover with the watch glass and weigh. The difference in weight before and after extraction represents the weight of fat. Calculate the percentage of fat present.

*Determination of Salt.* The powdery contents of the cup are made up of curd and mineral matter, the latter consisting almost entirely of salt. By means of warm water transfer the entire contents of the cup into a 250 ml. volumetric flask. Cool, bring the volume to the mark and thoroughly shake all the salt into solution.

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[1] *J. Dairy Sci.* 13, 380 (1930).

By means of a bulb pipette, transfer exactly 25.0 ml. of the well-mixed solution into a porcelain dish or beaker placed on a white surface. Add 25 ml. of distilled water, 2–3 drops of potassium chromate indicator, and titrate to the first permanent discernible red tinge with standard silver nitrate solution (Mohr method—see p. 108). From the milliliters of standard silver nitrate solution used and the weight of sample, calculate the percentage of sodium chloride in the butter.

*Remarks.* Since the mineral matter in butter is composed almost entirely of sodium chloride, the percentage of curd, for all practical purposes, may be obtained by subtracting the sum of the moisture, fat, and salt percentages from 100.

If the sample contains less than 80 per cent fat it does not meet the specifications for butter and must be reworked to meet the specifications before being offered for sale. An excessive curd content may indicate the addition of powdered milk to butter.

## ANALYSIS OF BUTTER FAT

The adulteration of butter fat with a cheaper foreign fat is detected by a determination of the physical and chemical numbers of the fat sample and comparison with the numbers for pure butter fat (Table 19). The differences in physical and chemical numbers between the different fats are due almost entirely to the amounts and kinds of the various fatty acid glycerides making up the fat. Butter fat is unique among all the naturally occurring fats in that it alone contains butyric acid glycerides. This makes possible the differentiation of butter fat from other common edible fats.

**Preparation of the Sample for Analysis.** Melt the sample at a temperature not exceeding 60° C. and permit the curd to separate from the fat. Decant only the fat through a filter paper placed in a water jacketed funnel heated to 70° C. collecting the filtered fat, free from water and curd, in a weighing bottle equipped with a medicine dropper. Any water passing through the filter with the fat may easily be observed in the liquid fat and will require the refiltering of the entire sample until entirely free from water.

**Refractive Index.** Obtaining this characteristic presents a simple accurate method for the rapid determination of the purity of a butter fat. The refractive index can be obtained readily by means of the Abbe refractometer (pp. 121–122). The reading is normally made at 40° C., or corrected to that temperature using the constant 0.000365 change in refractive index per degree C. change in the temperature.

TABLE 19. CHARACTERISTICS OF SOME COMMON SOLID AND LIQUID FATS

| Fat | Refractive Index at 25° C. | Melting Point ° C. | Saponification Number | Iodine Number | Reichert-Meissl Number | Polenske Number |
|---|---|---|---|---|---|---|
| Beef tallow | *1.4566–1.4596 | 43–48 | 194–200 | 35–43 | 0.2–0.5 | 0.5–0.6 |
| Butter fat | *1.4538–1.4562 | 30–35 | 220–233 | 26–35 | 20–32 | 1.2–2.4 |
| Castor oil | 1.4762–1.4776 | | 178–188 | 80–88 | 0.2–0.3 | |
| Cacao butter | *1.4563–1.4575 | 28–33 | 193–198 | 33–39 | 0.3–1.0 | |
| Coconut oil | 1.4523–1.4563 | 20–28 | 245–262 | 7–10 | 6–9 | 15–20 |
| Cod liver oil | 1.4755–1.4800 | | 175–190 | 136–170 | | |
| Corn oil | 1.4710–1.4740 | | 186–196 | 115–130 | 0.3–0.4 | |
| Cottonseed oil | 1.4696–1.4718 | | 192–196 | 102–112 | 0.7–0.9 | |
| Fanweed seed oil | *1.4671 | | 178 | 117 | 0.25 | |
| Lard | *1.4580–1.4620 | 36–45 | 195–200 | 55–67 | 0.2–0.6 | 0.4–0.6 |
| Lard oil | 1.4652–1.4676 | | 193–198 | 70–80 | | |
| Linseed oil | 1.4790–1.4816 | | 190–195 | 170–203 | | |
| Menhaden oil | 1.4760–1.4785 | | 188–193 | 148–180 | | |
| Mutton tallow | *1.4547–1.4587 | 44–48 | 193–196 | 32–60 | 0.3 | |
| Oleo oil | *1.4575–1.4595 | 30–39 | 198–202 | 40–50 | 0.3–0.4 | 0.5–0.6 |
| Olive oil | 1.4662–1.4681 | | 190–198 | 81–89 | 0.3–0.6 | |
| Palm kernel oil | *1.4495–1.4517 | 23–30 | 243–255 | 13–18 | 4–8 | 7–12 |
| Palm oil | *1.4537–1.4570 | 28–48 | 196–205 | 49–58 | 0.8–1.6 | |
| Peanut oil | 1.4684–1.4718 | | 186–194 | 88–98 | 0.4–0.5 | |
| Rape seed oil | 1.4702–1.4713 | | 172–180 | 98–106 | | |
| Sesame seed oil | 1.4704–1.4717 | | 188–193 | 105–115 | 1.0–1.2 | |
| Soy bean oil | 1.4724–1.4736 | | 190–196 | 126–136 | | |
| Sunflower seed oil | 1.4710–1.4740 | | 188–194 | 120–134 | 0.3–0.5 | |
| Tea seed oil | 1.4683–1.4703 | | 190–195 | 80–87 | | |
| Tung oil | 1.5181–1.5231 | | 190–196 | 160–170 | | |
| Whale oil | 1.4711–1.4730 | | 180–200 | 130–142 | | |
| White mustard seed oil | 1.4680–1.4714 | | 171–176 | 93–105 | | |

* Refractive index at 40° C.

Butter and coconut fat have comparatively low refractive indices because the fatty acids present in their glycerides are more saturated, with many of them of shorter chain length than those found in other fats. Butyric acid glycerides are found only in butter while caproic, caprylic, and capric acids are found in coconut and palm kernel oil. In these three fats the saturated acid glycerides greatly predominate. Most of the other fats consist principally of the glycerides of the 16 and 18 carbon saturated and unsaturated acids. In these, oleic acid glycerides generally account for the unsaturation in the solid fats, while linoleic and linolenic acids are usually present in the glycerides of the liquid fats.

Determine the refractive index of the butter fat sample at 40° C., using the Abbe refractometer. Compare the value obtained with the normal for butter fat found in Table 19, page 225.

**Melting Point.** This characteristic is useful in detecting the admixture of a foreign fat with butter. Coconut fat and the liquid fats if mixed with butter fat would lower the melting point. The solid fats if mixed with butter fat will maintain or tend to raise the melting point. Determine the melting point of the butter fat by the capillary tube method and compare the value obtained with the normal found in Table 19, page 225.

*Capillary Tube Method.* The fat is liquefied, a sample drawn into a capillary tube, and stored for the required time at 3°–10° C. The tube is then attached to a thermometer, placed in a water bath that is heated gradually, and the temperature at which the fat in the tube melts is ascertained.

*Procedure.* A thin-walled capillary tube, approximately 8 cm. long and 1 mm. in diameter, is drawn from a piece of thin-walled glass tubing. The fat is melted and a sample drawn into the tube to a height of 1 cm. by capillarity, after which the lower end of the tube is sealed off in a flame. The tube and contents are then stored in a refrigerator (3°–10° C.) for 18 hours or longer.

Upon removal from the refrigerator, the capillary tube containing the sample is fastened to a thermometer with a rubber band in such a manner that the fat sample is on a level with the bulb of the thermometer. For accurate readings, a thermometer graduated in tenths of a degree is necessary. Suspend the thermometer and attached capillary tube in a test tube containing water so that the water covers the bulb of the thermometer to a height of 3 cm. Suspend the test tube in another vessel—a beaker or flask—also containing water to a height equal to that in the test tube. Heat the water gradually in the outer vessel so that the temperature change is approximately 0.5° C. per minute. Continue the gradual heating until the fat sample melts, as is evidenced by a change from an opaque to a transparent appearance. Several determinations should be made and the mean taken as the melting point.

*Remarks.* When a fat solidifies after being in the liquid state, unstable crystal structures are formed which pass over into a stable form with time. Since these two crystal forms of the fat do not have the same melting point, it is necessary to insure that the fat sample used in determining the melting point has crystallized into the stable form. This is insured by storing the fat samples for 18 hours, or longer, at refrigerator temperatures previous to the actual determination.

**Saponification Number.** The saponification number is the number of milligrams of potassium hydroxide required to saponify one gram of fat. This characteristic is an index of the mean molecular weight of the fatty acid glycerides comprising a fat. Butter fat, coconut, and palm kernel oils contain appreciable quantities of short chain fatty acid glycerides and have comparatively high saponification numbers. All other animal and vegetable fats are comprised primarily of long chain fatty acid glycerides and consequently have lower saponification numbers. Thus it is possible to use this characteristic to determine the admixture of a foreign fat with butter fat.

A weighed sample of the fat is treated with a measured volume of alcoholic potassium hydroxide solution and saponified by heating. The excess potassium hydroxide is back-titrated with standard 0.5 N acid, using phenolphthalein as indicator. A blank determination is run simultaneously with the sample to determine the concentration of the alcoholic potassium hydroxide solution. From the titration values on the blank and the samples, calculate the saponification number of the butter fat and compare the value obtained with the normal found in Table 19, page 225.

*Reagents.*

1. *Approximately 0.7 N aldehyde-free alcoholic potassium hydroxide solution.* Reflux a mixture of 1,200 ml. of 95 per cent ethyl alcohol, 10 grams of potassium hydroxide, and 6 grams of aluminum foil for 30 min. Distill and collect 1 liter of the alcohol after discarding the first 50 ml. coming over. Pipette 50 ml. of a saturated potassium hydroxide solution into a liter volumetric flask and dilute to volume with the prepared aldehyde-free alcohol.
2. *Standard 0.5 N acid solution.*
3. *Phenolphthalein indicator solution or Alkali-Blue 6B indicator solution.* The latter is prepared by saturating 100 ml. of 95 per cent ethyl alcohol solution with the dye and filtering.

*Procedure.* Melt the fat and transfer it to a small weighing bottle equipped with a medicine dropper. Weigh the bottle and fat, transfer by means of the medicine dropper approximately 5 grams of the fat to a 300 ml. Erlenmeyer flask, and re-weigh the weighing bottle and remaining fat. The weight of the fat sample is obtained by difference. Determinations should be made in duplicate.

Accurately measure 50.0 ml. of the alcoholic potassium hydroxide solution by means of a pipette or burette and add to the fat sample in the Erlenmeyer flask. Attach an air condenser to the top of the flask by means of a rubber stopper, and reflux on a steam bath for 30 min. Complete saponification of fats usually occurs within 15 min., so a 30-min. period is normally sufficient. However, if it is known that the material is difficult to saponify, a longer heating period may be necessary. Complete saponification has occurred when the solution is entirely homogeneous.

The flask is then cooled, 1 ml. of phenolphthalein indicator solution added, and the excess potassium hydroxide present determined by titration with standard 0.5 N acid solution. If the solution becomes reddish brown during the saponification, it is helpful to add 1 ml. of the Alkali-Blue 6B indicator solution in addition to the phenolphthalein before titrating. Phenolphthalein and Alkali-Blue 6B have the same color (red) in alkali solutions; but, whereas phenolphthalein is colorless in acid solution, the Alkali-Blue 6B is blue.

Two blank determinations are run simultaneously with the samples. The blank determinations contain the same volumes of alcoholic potassium hydroxide solution measured in the same way and are refluxed for the same length of time as the samples. The titration values obtained on the blanks determine the concentration of the potassium hydroxide solution and so are just as essential as the samples.

*Remarks.* Aldehyde-free alcohol is used for the preparation of the alcoholic potassium hydroxide solution so that a minimum amount of resinification with attendant color formation occurs during the saponification of the fat. Saturated potassium hydroxide is used so that carbonates will be eliminated in the preparation of the alcoholic potassium hydroxide solution. Carbonates would later interfere with the titration since phenolphthalein is used as an indicator.

An air condenser is used to prevent the loss of alcohol during saponification. It is necessary that at the end of the titration an approximately 50 per cent alcohol solution remains in order to prevent hydrolysis of the potassium soaps present. If less than the required amount of alcohol is present, an incorrect titration value is obtained. If alcohol is lost during the saponification, sufficient neutral aldehyde-free alcohol should be added to give the required 50 per cent alcohol concentration at the end of the titration.

*Calculation.* When exactly the same volume of alcoholic potassium hydroxide solution was used in the blank as in the sample, the following formula may be used to calculate the Saponification Number (Sap. No.):

$$\text{Sap. No.} = \frac{(\text{Blank titration} - \text{Sample titration}) \times \text{N.F. acid} \times 0.0561 \times 1000}{\text{Sample weight in grams}}.$$

**Free Fatty Acid Number.** This is defined as the number of milligrams of potassium hydroxide required to neutralize the free fatty acids present in one gram of fat. This number is a measure of the amount of fatty acids which have been freed by hydrolysis from their glyceride combination through the action of water, temperature, and lipolytic enzymes. In other words, it is a measure of the degree of hydrolytic rancidity undergone by the butter fat, indicative of the relative quality of the fat. This number is of no value in determining the admixture of a foreign fat with butter fat.

A sample of butter fat, weighed to the nearest tenth of a gram, is suspended in hot ethyl alcohol, and the free fatty acids present titrated with a standard 0.1 N alkali solution using phenolphthalein as indicator. From the titration value, calculate the free fatty acid number of the butter fat.

*Reagents.*

1. *Standard 0.1 N sodium hydroxide solution.*
2. *Phenolphthalein indicator solution* (see p. 72).

*Procedure.* Weigh 10–20 grams of the butter fat into a 300 ml. Erlenmeyer flask and add 50 ml. of ethyl alcohol. Heat the mixture to boiling on the steam bath, remove, and immediately titrate the free acids with standard 0.1 N alkali solution using phenolphthalein as indicator. Shake the flask thoroughly throughout the titration and stop the addition of standard alkali solution when a detectable pink color persists for 1 min.

Run a blank determination on the same volume of ethyl alcohol and determine the volume of standard 0.1 N alkali solution required to give a detectable pink color with phenolphthalein which will persist for 1 min. Subtract this blank determination from the titration value obtained on the sample to determine the true volume of standard alkali solution required to neutralize the free fatty acids present in the sample.

The ethyl alcohol dissolves the free fatty acids and furnishes the medium in which the titration with standard alkali takes place. The alcohol also prevents the hydrolysis of the soaps formed during the titration.

*Calculation.* The following formula may be used to calculate the Free Fatty Acid Number (F.F.A. No.):

$$\text{F.F.A. No.} = \frac{(\text{Sample titration} - \text{Blank titration}) \times \text{N.F. alkali} \times 0.0561 \times 1000}{\text{Sample weight in grams}}.$$

**Iodine Number—Wiji Method.**[1] The iodine number is the number of grams of iodine absorbed by 100 grams of fat. This characteristic is a measure of the unsaturated linkages present in the fat. Coconut fat has an exceptionally low iodine number (7–10) which is very useful in its identification. Butter fat and oleo oil have comparatively low iodine numbers (28–40), due principally to the oleic acid glycerides which they contain. Practically all the other edible animal and vegetable fats have iodine numbers ranging from 65 to 130. In general, solid fats have lower iodine numbers than the liquid fats. This characteristic then is useful in determining the presence and, to some extent, the identity of a foreign fat when mixed with butter fat.

The general procedure involved in an iodine number determination is as follows: A weighed sample of fat is dissolved in chloroform and treated with a measured volume of halogen solution in a special glass-stoppered iodine flask. The halogen solution added must contain 100–150 per cent excess halogenating agent to obtain the proper results. This is accomplished by decreasing the size of the fat sample in proportion to its expected unsaturation. The flask and contents are stored for sufficient time to permit the addition of halogen to the unsaturated glycerides and then the excess halogen solution is back-titrated with standard 0.1 N sodium thiosulfate solution. A blank determination is run simultaneously with the samples to determine the concentration of the halogenating agent. The amount of halogen reacting with the unsaturated glycerides is calculated as iodine. Compare the iodine number obtained on the butter fat with the normal found in Table 19, page 225.

*Reagents.*

1. *Wiji's iodine solution.* Dissolve 13 grams of resublimed iodine in 1 liter of glacial acetic acid (99.5 per cent and showing no reduction with potassium dichromate) using heat, if desired, to effect a more rapid solution of the iodine. Cool

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[1] Wÿs, *Ber.*, **31**, 750 (1898).

the solution and titrate a 20.0 ml. portion with standard 0.1 N sodium thiosulfate solution. Pour a small portion of the iodine solution into a beaker and pass washed and dried chlorine gas into the main portion of the solution until the original titration figure is doubled. Pour the small portion of the original iodine solution into the chlorinated solution, which should reduce the chlorine content of the entire solution to slightly less than that of the iodine content. It is desired that, in the chlorination, the halogen content be almost, but not quite, doubled. An excess of iodine is necessary in the solution but an excess of chlorine must be avoided.

2. *A potassium iodide solution* containing 15 grams of potassium iodide dissolved in 85 ml. of water.
3. *A standard 0.1 N sodium thiosulfate solution.*
4. *Starch indicator solution* (p. 101).

*Procedure.* Weigh accurately about 0.5 gram of the butter fat into a 300 ml. glass-stoppered iodine flask. Dissolve the fat in 15 ml. of chloroform. Add 25 ml. of the Wiji iodine solution from a pipette or preferably from a glass-stoppered burette. Stopper the flask and place in the desk for 30 min. At the end of this time, loosen the stopper and wash it off into the flask with 20 ml. of the 15 per cent potassium iodide solution followed by 100 ml. of water. Titrate the iodine solution with standard 0.1 N sodium thiosulfate solution until the yellow iodine color has almost disappeared. Add a few drops of starch indicator solution and continue the titration to the disappearance of the blue color. Near the end of the titration, stopper the flask and shake vigorously after each small addition of the standard thiosulfate solution to get all the iodine held in the chloroform layer into the water phase, where it can react with the thiosulfate.

Two blank determinations are run simultaneously with the samples. The same quantities of reagents are used as in the samples and the volumes measured with the same volumetric apparatus. The average value obtained for the blank determinations is used to ascertain the halogen concentration of the Wiji iodine solution.

*Calculation.* When exactly the same volume of iodine solution was used in the blank as in the sample, the following formula may be used to calculate the Iodine Number (I. No.):

$$\text{I. No.} = \frac{(\text{Blank titration} - \text{Sample titration}) \times \text{N.F. } Na_2S_2O_3 \times 0.1269 \times 100}{\text{Sample weight in grams}}.$$

**Reichert-Meissl and Polenske Numbers.** The Reichert-Meissl number is defined as the number of milliliters of 0.1 N alkali solution required to neutralize the volatile soluble fatty acids distilled from 5 grams of fat. The Polenske number is the number of milliliters of 0.1 N alkali solution required to neutralize the volatile insoluble fatty acids distilled from 5 grams of fat.

These determinations have been used principally for the analysis of butter and oleomargarines. Butterfat contains appreciable quantities of butyric acid glycerides. Butyric acid is volatile and soluble in water. No other fat contains butyric acid glycerides, therefore the Reichert-Meissl number of butterfat is higher than that for any other fat. Coconut oil and palm kernel oil contain appreciable quantities of caproic, caprylic, capric, and lauric acid glycerides. These fatty acids are somewhat volatile with steam but are not appreciably soluble in water. For this reason, coconut and palm kernel oil have a fairly low Reichert-Meissl number but a high Polenske number. The other commonly occurring fats do not contain appreciable quantities of fatty acid glycerides below lauric acid and, consequently, have very low Reichert-Meissl and Polenske numbers.

A weighed sample of fat is saponified and the soaps formed treated with sulfuric acid, liberating the free fatty acids. The mixture is distilled in a current of steam under empirical conditions and the volatile fatty acids collected in 110 ml. of distillate. The distillate is filtered, separating the soluble from the insoluble acids. The Reichert-Meissl number is determined by titrating the soluble acids in the filtrate. The Polenske number is obtained by dissolving the insoluble acids in alcohol and titrating with standard alkali solution.

*Reagents.*

1. *Glycerol-soda solution.* Add 20 ml. of a clear saturated solution of sodium hydroxide to 180 ml. of glycerol.
2. *Dilute sulfuric acid solution.* To 4 volumes of water add 1 volume of concentrated sulfuric acid.
3. *Treated pumice stone.* Heat small pieces of pumice stone to a white heat in the flame of a burner, plunge into water, and keep there until used.

*Procedure.* Weigh accurately about 5 grams of the melted fat into a 300 ml. Florence flask, add 20 ml. of the glycerol-soda solution, and heat over a flame until the solution becomes clear, indicating complete saponification. It is preferable to rotate the flask while heating as this prevents excessive foaming and possible loss of the sample. Usually the saponification is complete with about 5 min. of heating directly over a flame.

Add 135 ml. of recently boiled distilled water, slowly at first to prevent foaming, then add 10 ml. of the dilute sulfuric acid solution and a few pieces of the treated pumice stone.

Distill the fatty acids in an apparatus having the approximate dimensions illustrated in Fig. 46. Support the flask on an asbestos board having a 2½-in. hole in the center. Regulate the flame so as to obtain 110 ml. of distillate in as near 30 min. as possible. Insure that the temperature of the distillate does not go above 20° C., and, if necessary, use a bath to control the temperature. As soon as the 110 ml. of distillate have been collected, remove the flame and substitute a 25 ml. graduated cylinder for the volumetric flask to collect the few drops of distillate which come over after the flame has been removed.

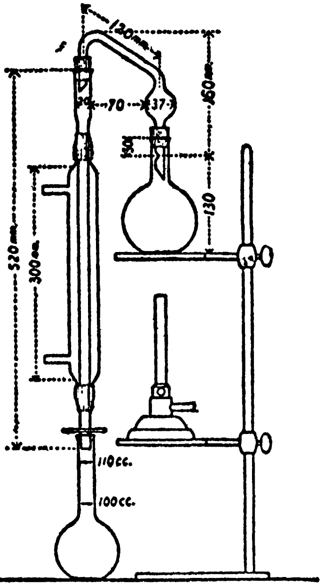

FIG. 46. Reichert-Meissl Polenske Apparatus. (From Association of Official Agricultural Chemists' "Methods of Analysis.")

Mix the distillate without shaking violently and immerse the flask almost completely in a water bath at 15° C. for 15 min. Filter the entire distillate through a 9 cm. filter paper supported in a funnel, and titrate a 100 ml. aliquot of the filtrate with standard 0.1 N sodium hydroxide solution using phenolphthalein as indicator. A blank determination, using all the reagents and the same technique throughout as was used on the samples, is run simultaneously with the samples.

The Reichert-Meissl number is the titration figure obtained, calculated to a 5 gram fat sample, multiplied by 1.1 and corrected for the blank titration.

Disconnect the flask and distilling head from the condenser. Pass three successive 15 ml. portions of water through first the condenser, then the 25 ml. graduated cylinder, the 110 ml. volumetric flask, and finally the filter funnel. These three successive washings should remove all the soluble fatty acids remaining in the apparatus and the filter. Discard these water washings.

Dissolve the insoluble fatty acids by passing three successive 15 ml. portions of neutral alcohol through the apparatus and funnel as was done in the washing procedure. Collect all the neutral alcohol washings and titrate them with standard 0.1 N sodium hydroxide solution using phenolphthalein as indicator.

The Polenske number is the titration figure obtained calculated to an exactly 5 gram sample of fat.

*Remarks.* The determination of the Reichert-Meissl and Polenske numbers is highly empirical, since only a fraction of the volatile acids distill over with steam and are collected in the 110 ml. of distillate (approximately 80 per cent of the butyric and 25 per cent of the caprylic acids distill over). It is evident, then, since any change in procedure or in construction of the apparatus will influence the amount of acids distilled, that results are of value only if all the directions are followed as completely as possible.

*Interpretation of Results.* If the Reichert-Meissl number found deviates from the normal for butterfat (Table 19), and adulteration with a foreign fat other than coconut or palm kernel oil is indicated, calculate the percentage of adulterant present using the following formula:

$$XR_1 = 100\,R_3 - (100 - X)\,R_2,$$

where

$X$ = per cent of margarine fat;
$R_1$ = average Reichert-Meissl number of margarine fat;
$R_2$ = average Reichert-Meissl number of butterfat;
$R_3$ = Reichert-Meissl number of the sample.

If the Polenske number found deviates from the normal for butterfat (Table 19) and adulteration with coconut or palm kernel oil is indicated, calculate the percentage of adulterant present using the above formula, substituting Polenske numbers for each of the respective Reichert-Meissl numbers.

# CHAPTER XIV

# MAPLE SYRUP

Maple syrup is made by concentrating the sap of the live maple tree, or by the solution of a maple concrete. It contains not more than 35 per cent of water and weighs not less than 11 lbs. to the gallon.

Maple sap, as obtained from the maple tree, is a solution containing 1 to 6 per cent sucrose with small amounts of soluble protein matter, organic salts and organic acids.[1] In its concentration to syrup, most of the protein matter is coagulated and removed. A considerable portion of the organic salts also precipitate out and are removed. A slight hydrolysis of the sucrose occurs, either previous to or during the concentration of the sap, so that a small amount of invert sugar is normally present in the finished syrup. Very small amounts of ether soluble materials in the sap produce the characteristic maple flavor during the concentration process. The flavor depends to a great extent on an unstable phenolic substance which is associated with a crystalline aldehyde melting at 74°–76° C., and similar in odor and properties to vanillin.[2] While maple sap itself contains no lead, minute amounts of this metal

TABLE 20. COMPOSITION AND ANALYTICAL VALUES OF MAPLE SYRUP ON THE ORIGINAL BASIS

| | Max. | Min. | Ave. |
|---|---|---|---|
| Moisture, per cent | 50.4 | 26.7 | 33.1 |
| Sucrose, per cent | 70.0 | 44.1 | 60.8 |
| Invert sugar, per cent | 15.9 | 0.0 | 2.7 |
| Total ash, per cent | 1.10 | 0.38 | 0.55 |
| Soluble ash, per cent | 0.77 | 0.21 | 0.40 |
| Insoluble ash, per cent | 0.65 | 0.14 | 0.24 |
| Sol. ash ÷ Insol. ash | 3.96 | 0.48 | 1.70 |
| Alkalinity of soluble ash | 8.50 | 2.74 | 4.88 |
| Alkalinity of insoluble ash | 12.94 | 2.34 | 5.98 |
| Alk. sol. ash ÷ alk. insol. ash | 2.06 | 0.29 | 0.82 |
| Winton lead number | 2.91 | 1.20 | 1.60 |

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[1] Nelson, *J. Amer. Chem. Soc.*, 50, 2006 (1928).

[2] Nelson, *J. Amer. Chem. Soc.*, 50, 2009 (1928).

may find its way into the commercial syrups from the collecting pails and evaporators used in obtaining the syrup.

Maple syrup is analyzed to determine if it conforms to the established standard of composition and to show that it has not been adulterated by the substitution of a sugar for maple sugar. The analyses discussed under maple syrup are applicable also to other sugar products. The average composition and analytical values for maple syrup are given in Table 20.

**Preparation of Sample for Analysis.** If sugar has crystallized out of solution, redissolve the crystals by heating. Other insoluble matter which does not redissolve on heating should be filtered off through cotton wool.

**Moisture Determination.** Moisture in sugar products may be determined by loss in weight on heating, by the refractometer, or by specific gravity methods. Special care is required when applying drying methods to sugar products due to the possibility of caramelizing the sugars. Refractometric and specific gravity methods are much more rapid and simple. However, slight errors may be introduced in these methods due to the presence of soluble materials other than sugars.

*Loss in Weight on Drying.* Place 15–20 grams of clean ignited quartz sand and a short stirring rod in a dish approximately 55 mm. in diameter and 40 mm. deep, fitted with a cover. Dry the dish and contents thoroughly, cover the dish, cool in a desiccator, and weigh immediately after cooling. Accurately weigh a syrup sample of 2–3 grams into the dish and add enough water to mix sample thoroughly with the sand. Heat on the steam bath for 15–20 min., stirring at intervals until the mass becomes too stiff to stir readily. Dry in a vacuum oven at 70° C. to constant weight. Start weighing at the end of an initial 10–12 hour heating period and weigh at 2 hour intervals thereafter until constant weight is obtained. Weigh the covered dish and contents immediately after cooling in the desiccator as the dried material is very hygroscopic. Calculate the percentage of moisture present.

*Refractometer Method.* Determine the refractive index of the syrup at 20° C. with an Abbe refractometer (see pp. 121–122) and obtain the corresponding percentage of dry matter (as sucrose) from Table 21. If the readings are made at temperatures other than 20° C. apply the corrections in Table 22, and obtain the percentage of dry matter.

*Hydrometer Method.* In routine control work involving sugar products, the hydrometer method is commonly used for the de-

Table 21.* Refractive Indices of Sucrose Solutions at 20° C.†
(International Scale, 1936)‡

| Refractive Index at 20° | Sucrose, Per Cent | Refractive Index at 20° | Sucrose, Per Cent | Refractive Index at 20° | Sucrose, Per Cent | Refractive Index at 20° | Sucrose, Per Cent | Refractive Index at 20° | Sucrose, Per Cent |
|---|---|---|---|---|---|---|---|---|---|
| 1.33299 | 0.0 | 1.34629 | 9.0 | 1.36053 | 18.0 | 1.3758 | 27.0 | 1.3920 | 36.0 |
| .33328 | 0.2 | .34660 | 9.2 | .36086 | 18.2 | .3761 | 27.2 | .3924 | 36.2 |
| .33357 | 0.4 | .34691 | 9.4 | .36119 | 18.4 | .3765 | 27.4 | .3928 | 36.4 |
| .33385 | 0.6 | .34721 | 9.6 | .36152 | 18.6 | .3768 | 27.6 | .3931 | 36.6 |
| .33414 | 0.8 | .34752 | 9.8 | .36185 | 18.8 | .3772 | 27.8 | .3935 | 36.8 |
| .33443 | 1.0 | .34783 | 10.0 | .36218 | 19.0 | .3775 | 28.0 | .3939 | 37.0 |
| .33472 | 1.2 | .34814 | 10.2 | .36251 | 19.2 | .3779 | 28.2 | .3943 | 37.2 |
| .33501 | 1.4 | .34845 | 10.4 | .36284 | 19.4 | .3782 | 28.4 | .3947 | 37.4 |
| .33530 | 1.6 | .34875 | 10.6 | .36318 | 19.6 | .3786 | 28.6 | .3950 | 37.6 |
| .33559 | 1.8 | .34906 | 10.8 | .36351 | 19.8 | .3789 | 28.8 | .3954 | 37.8 |
| .33588 | 2.0 | .34937 | 11.0 | .36384 | 20.0 | .3793 | 29.0 | .3958 | 38.0 |
| .33617 | 2.2 | .34968 | 11.2 | .36417 | 20.2 | .3797 | 29.2 | .3962 | 38.2 |
| .33646 | 2.4 | .34999 | 11.4 | .36451 | 20.4 | .3800 | 29.4 | .3966 | 38.4 |
| .33675 | 2.6 | .35031 | 11.6 | .36484 | 20.6 | .3804 | 29.6 | .3970 | 38.6 |
| .33704 | 2.8 | .35062 | 11.8 | .36518 | 20.8 | .3807 | 29.8 | .3974 | 38.8 |
| .33733 | 3.0 | .35093 | 12.0 | .36551 | 21.0 | .3811 | 30.0 | .3978 | 39.0 |
| .33762 | 3.2 | .35124 | 12.2 | .36585 | 21.2 | .3815 | 30.2 | .3982 | 39.2 |
| .33792 | 3.4 | .35156 | 12.4 | .36618 | 21.4 | .3818 | 30.4 | .3986 | 39.4 |
| .33821 | 3.6 | .35187 | 12.6 | .36652 | 21.6 | .3822 | 30.6 | .3989 | 39.6 |
| .33851 | 3.8 | .35219 | 12.8 | .36685 | 21.8 | .3825 | 30.8 | .3993 | 39.8 |
| .33880 | 4.0 | .35250 | 13.0 | .36719 | 22.0 | .3829 | 31.0 | .3997 | 40.0 |
| .33909 | 4.2 | .35282 | 13.2 | .36753 | 22.2 | .3833 | 31.2 | .4001 | 40.2 |
| .33939 | 4.4 | .35313 | 13.4 | .36787 | 22.4 | .3836 | 31.4 | .4005 | 40.4 |
| .33968 | 4.6 | .35345 | 13.6 | .36820 | 22.6 | .3840 | 31.6 | .4008 | 40.6 |
| .33998 | 4.8 | .35376 | 13.8 | .36854 | 22.8 | .3843 | 31.8 | .4012 | 40.8 |
| .34027 | 5.0 | .35408 | 14.0 | .36888 | 23.0 | .3847 | 32.0 | .4016 | 41.0 |
| .34057 | 5.2 | .35440 | 14.2 | .36922 | 23.2 | .3851 | 32.2 | .4020 | 41.2 |
| .34087 | 5.4 | .35472 | 14.4 | .36956 | 23.4 | .3854 | 32.4 | .4024 | 41.4 |
| .34116 | 5.6 | .35503 | 14.6 | .36991 | 23.6 | .3858 | 32.6 | .4028 | 41.6 |
| .34146 | 5.8 | .35535 | 14.8 | .37025 | 23.8 | .3861 | 32.8 | .4032 | 41.8 |
| .34176 | 6.0 | .35567 | 15.0 | .37059 | 24.0 | .3865 | 33.0 | .4036 | 42.0 |
| .34206 | 6.2 | .35599 | 15.2 | .3709 | 24.2 | .3869 | 33.2 | .4040 | 42.2 |
| .34236 | 6.4 | .35631 | 15.4 | .3713 | 24.4 | .3872 | 33.4 | .4044 | 42.4 |
| .34266 | 6.6 | .35664 | 15.6 | .3716 | 24.6 | .3876 | 33.6 | .4048 | 42.6 |
| .34296 | 6.8 | .35696 | 15.8 | .3720 | 24.8 | .3879 | 33.8 | .4052 | 42.8 |
| .34326 | 7.0 | .35728 | 16.0 | .3723 | 25.0 | .3883 | 34.0 | .4056 | 43.0 |
| .34356 | 7.2 | .35760 | 16.2 | .3726 | 25.2 | .3887 | 34.2 | .4060 | 43.2 |
| .34386 | 7.4 | .35793 | 16.4 | .3730 | 25.4 | .3891 | 34.4 | .4064 | 43.4 |
| .34417 | 7.6 | .35825 | 16.6 | .3733 | 25.6 | .3894 | 34.6 | .4068 | 43.6 |
| .34447 | 7.8 | .35858 | 16.8 | .3737 | 25.8 | .3898 | 34.8 | .4072 | 43.8 |
| .34477 | 8.0 | .35890 | 17.0 | .3740 | 26.0 | .3902 | 35.0 | .4076 | 44.0 |
| .34507 | 8.2 | .35923 | 17.2 | .3744 | 26.2 | .3906 | 35.2 | .4080 | 44.2 |
| .34538 | 8.4 | .35955 | 17.4 | .3747 | 26.4 | .3909 | 35.4 | .4084 | 44.4 |
| .34568 | 8.6 | .35988 | 17.6 | .3751 | 26.6 | .3913 | 35.6 | .4088 | 44.6 |
| .34599 | 8.8 | .36020 | 17.8 | .3754 | 26.8 | .3916 | 35.8 | .4092 | 44.8 |

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* From the Assoc. Off. Agr. Chem., "Methods of Analysis" (1940).

† This table is in accordance with the International Scale of Refractive Indices of Sucrose Solutions at 20° C. 1936, adopted as official (final action) at the

TABLE 21. *Continued.*

| Refractive Index at 20° | Sucrose, Per Cent | Refractive Index at 20° | Sucrose, Per Cent | Refractive Index at 20° | Sucrose, Per Cent | Refractive Index at 20° | Sucrose, Per Cent | Refractive Index at 20° | Sucrose, Per Cent |
|---|---|---|---|---|---|---|---|---|---|
| 1.4096 | 45.0 | 1.4264 | 53.0 | 1.4441 | 61.0 | 1.4627 | 69.0 | 1.4825 | 77.0 |
| .4100 | 45.2 | .4268 | 53.2 | .4446 | 61.2 | .4631 | 69.2 | .4830 | 77.2 |
| .4104 | 45.4 | .4272 | 53.4 | .4450 | 61.4 | .4636 | 69.4 | .4835 | 77.4 |
| .4109 | 45.6 | .4277 | 53.6 | .4455 | 61.6 | .4641 | 69.6 | .4840 | 77.6 |
| .4113 | 45.8 | .4281 | 53.8 | .4459 | 61.8 | .4646 | 69.8 | .4845 | 77.8 |
| .4117 | 46.0 | .4285 | 54.0 | .4464 | 62.0 | .4651 | 70.0 | .4850 | 78.0 |
| .4121 | 46.2 | .4289 | 54.2 | .4468 | 62.2 | .4656 | 70.2 | .4855 | 78.2 |
| .4125 | 46.4 | .4294 | 54.4 | .4473 | 62.4 | .4661 | 70.4 | .4860 | 78.4 |
| .4129 | 46.6 | .4298 | 54.6 | .4477 | 62.6 | .4666 | 70.6 | .4865 | 78.6 |
| .4133 | 46.8 | .4303 | 54.8 | .4482 | 62.8 | .4671 | 70.8 | .4871 | 78.8 |
| .4137 | 47.0 | .4307 | 55.0 | .4486 | 63.0 | .4676 | 71.0 | .4876 | 79.0 |
| .4141 | 47.2 | .4311 | 55.2 | .4491 | 63.2 | .4681 | 71.2 | .4881 | 79.2 |
| .4145 | 47.4 | .4316 | 55.4 | .4495 | 63.4 | .4685 | 71.4 | .4886 | 79.4 |
| .4150 | 47.6 | .4320 | 55.6 | .4500 | 63.6 | .4690 | 71.6 | .4891 | 79.6 |
| .4154 | 47.8 | .4325 | 55.8 | .4504 | 63.8 | .4695 | 71.8 | .4896 | 79.8 |
| .4158 | 48.0 | .4329 | 56.0 | .4509 | 64.0 | .4700 | 72.0 | .4901 | 80.0 |
| .4162 | 48.2 | .4333 | 56.2 | .4514 | 64.2 | .4705 | 72.2 | .4906 | 80.2 |
| .4166 | 48.4 | .4338 | 56.4 | .4518 | 64.4 | .4710 | 72.4 | .4912 | 80.4 |
| .4171 | 48.6 | .4342 | 56.6 | .4523 | 64.6 | .4715 | 72.6 | .4917 | 80.6 |
| .4175 | 48.8 | .4347 | 56.8 | .4527 | 64.8 | .4720 | 72.8 | .4922 | 80.8 |
| .4179 | 49.0 | .4351 | 57.0 | .4532 | 65.0 | .4725 | 73.0 | .4927 | 81.0 |
| .4183 | 49.2 | .4355 | 57.2 | .4537 | 65.2 | .4730 | 73.2 | .4933 | 81.2 |
| .4187 | 49.4 | .4360 | 57.4 | .4541 | 65.4 | .4735 | 73.4 | .4938 | 81.4 |
| .4192 | 49.6 | .4364 | 57.6 | .4546 | 65.6 | .4740 | 73.6 | .4943 | 81.6 |
| .4196 | 49.8 | .4369 | 57.8 | .4550 | 65.8 | .4744 | 73.8 | .4949 | 81.8 |
| .4200 | 50.0 | .4373 | 58.0 | .4555 | 66.0 | .4749 | 74.0 | .4954 | 82.0 |
| .4204 | 50.2 | .4378 | 58.2 | .4560 | 66.2 | .4754 | 74.2 | .4959 | 82.2 |
| .4208 | 50.4 | .4382 | 58.4 | .4565 | 66.4 | .4759 | 74.4 | .4964 | 82.4 |
| .4213 | 50.6 | .4387 | 58.6 | .4569 | 66.6 | .4764 | 74.6 | .4970 | 82.6 |
| .4217 | 50.8 | .4391 | 58.8 | .4574 | 66.8 | .4769 | 74.8 | .4975 | 82.8 |
| .4221 | 51.0 | .4396 | 59.0 | .4579 | 67.0 | .4774 | 75.0 | .4980 | 83.0 |
| .4225 | 51.2 | .4400 | 59.2 | .4584 | 67.2 | .4779 | 75.2 | .4985 | 83.2 |
| .4229 | 51.4 | .4405 | 59.4 | .4589 | 67.4 | .4784 | 75.4 | .4991 | 83.4 |
| .4234 | 51.6 | .4409 | 59.6 | .4593 | 67.6 | .4789 | 75.6 | .4996 | 83.6 |
| .4238 | 51.8 | .4414 | 59.8 | .4598 | 67.8 | .4794 | 75.8 | .5001 | 83.8 |
| .4242 | 52.0 | .4418 | 60.0 | .4603 | 68.0 | .4799 | 76.0 | .5007 | 84.0 |
| .4246 | 52.2 | .4423 | 60.2 | .4607 | 68.2 | .4804 | 76.2 | .5012 | 84.2 |
| .4251 | 52.4 | .4427 | 60.4 | .4612 | 68.4 | .4810 | 76.4 | .5017 | 84.4 |
| .4255 | 52.6 | .4432 | 60.6 | .4617 | 68.6 | .4815 | 76.6 | .5022 | 84.6 |
| .4260 | 52.8 | .4436 | 60.8 | .4622 | 68.8 | .4820 | 76.8 | .5028 | 84.8 |
| | | | | | | | | .5033 | 85.0 |

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1938 meeting of the Association. The values of the indices for the range 0–24 per cent sucrose are given to five decimal places instead of to four. This arrangement is desirable when the table is used with refractometers capable of readings to the fifth place. The values for whole per cents of sucrose are those of the International Scale; the remaining fractional values are obtained by interpolation. The values of indices above 24 per cent sucrose are identical with those in Table 6, "Methods of Analysis," Assoc. Off. Agr. Chem., 1935, p. 622.

‡ *Intern. Sugar J.*, 39, 22s (1937).

TABLE 22.* TABLE OF CORRECTIONS FOR DETERMINING PERCENTAGE OF SUCROSE IN SUGAR SOLUTIONS BY MEANS OF EITHER ABBÉ OR IMMERSION REFRACTOMETER WHEN READINGS ARE MADE AT TEMPERATURES OTHER THAN 20° C.†

(International Temperature Correction Table, 1936)†

| Temp. °C. | Per Cent Sucrose | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 40 | 50 | 60 | 70 |
| | *Subtract from the Per Cent Sucrose* | | | | | | | | | | |
| 10 | 0.50 | 0.54 | 0.58 | 0.61 | 0.64 | 0.66 | 0.68 | 0.72 | 0.74 | 0.76 | 0.79 |
| 11 | .46 | .49 | .53 | .55 | .58 | .60 | .62 | .65 | .67 | .69 | .71 |
| 12 | .42 | .45 | .48 | .50 | .52 | .54 | .56 | .58 | .60 | .61 | .63 |
| 13 | .37 | .40 | .42 | .44 | .46 | .48 | .49 | .51 | .53 | .54 | .55 |
| 14 | .33 | .35 | .37 | .39 | .40 | .41 | .42 | .44 | .45 | .46 | .48 |
| 15 | .27 | .29 | .31 | .33 | .34 | .34 | .35 | .37 | .38 | .39 | .40 |
| 16 | .22 | .24 | .25 | .26 | .27 | .28 | .28 | .30 | .30 | .31 | .32 |
| 17 | .17 | .18 | .19 | .20 | .21 | .21 | .21 | .22 | .23 | .23 | .24 |
| 18 | .12 | .13 | .13 | .14 | .14 | .14 | .14 | .15 | .15 | .16 | .16 |
| 19 | .06 | .06 | .06 | .07 | .07 | .07 | .07 | .08 | .08 | .08 | .08 |
| | *Add to the Per Cent Sucrose* | | | | | | | | | | |
| 21 | 0.06 | 0.07 | 0.07 | 0.07 | 0.07 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 |
| 22 | .13 | .13 | .14 | .14 | .15 | .15 | .15 | .15 | .16 | .16 | .16 |
| 23 | .19 | .20 | .21 | .22 | .22 | .23 | .23 | .23 | .24 | .24 | .24 |
| 24 | .26 | .27 | .28 | .29 | .30 | .30 | .31 | .31 | .31 | .32 | .32 |
| 25 | .33 | .35 | .36 | .37 | .38 | .38 | .39 | .40 | .40 | .40 | .40 |
| 26 | .40 | .42 | .43 | .44 | .45 | .46 | .47 | .48 | .48 | .48 | .48 |
| 27 | .48 | .50 | .52 | .53 | .54 | .55 | .55 | .56 | .56 | .56 | .56 |
| 28 | .56 | .57 | .60 | .61 | .62 | .63 | .63 | .64 | .64 | .64 | .64 |
| 29 | .64 | .66 | .68 | .69 | .71 | .72 | .72 | .73 | .73 | .73 | .73 |
| 30 | .72 | .74 | .77 | .78 | .79 | .80 | .80 | .81 | .81 | .81 | .81 |

* From the Assoc. Off. Agr. Chem., "Methods of Analysis" (1940).

† *Intern. Sugar J.*, **39**, 24s (1937).

termination of solids. A special hydrometer, reading in percentage of sugar directly at 20° C. (degrees Brix), has been developed for sugar work. If the reading is made at a temperature other than 20° C., apply the correction found in Table 23.

Brix readings are based upon pure sucrose solutions. Pure solutions of other sugars do not differ appreciably in specific gravity from equal concentrations of sucrose; therefore the Brix hydrometer may be used to determine the concentration of pure sugar solutions

## TABLE 23.* TEMPERATURE CORRECTIONS TO READINGS OF SACCHAROMETERS (Standard at 20° C.)

(This table is calculated from the data on thermal expansion of sugar solutions by Plato,† and it is assumed that the instrument is of Jena 16 in. glass. The table should be used with caution and only for approximate results when the temperature differs much from the standard temperature or from the temperature of the surrounding air.)

| Temperature In Degrees Centigrade | Observed Percentage Of Sugar | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 | 70 |
| | *Subtract* | | | | | | | | | | | | | |
| 0 | 0.30 | 0.49 | 0.65 | 0.77 | 0.89 | 0.99 | 1.08 | 1.16 | 1.24 | 1.31 | 1.37 | 1.41 | 1.44 | 1.49 |
| 5 | 0.36 | 0.47 | 0.56 | 0.65 | 0.73 | 0.80 | 0.86 | 0.91 | 0.97 | 1.01 | 1.05 | 1.08 | 1.10 | 1.14 |
| 10 | 0.32 | 0.38 | 0.43 | 0.48 | 0.52 | 0.57 | 0.60 | 0.64 | 0.67 | 0.70 | 0.72 | 0.74 | 0.75 | 0.77 |
| 11 | 0.31 | 0.35 | 0.40 | 0.44 | 0.48 | 0.51 | 0.55 | 0.58 | 0.60 | 0.63 | 0.65 | 0.66 | 0.68 | 0.70 |
| 12 | 0.29 | 0.32 | 0.36 | 0.40 | 0.43 | 0.46 | 0.50 | 0.52 | 0.54 | 0.56 | 0.58 | 0.59 | 0.60 | 0.62 |
| 13 | 0.26 | 0.29 | 0.32 | 0.35 | 0.38 | 0.41 | 0.44 | 0.46 | 0.48 | 0.49 | 0.51 | 0.52 | 0.53 | 0.55 |
| 14 | 0.24 | 0.26 | 0.29 | 0.31 | 0.34 | 0.36 | 0.38 | 0.40 | 0.41 | 0.42 | 0.44 | 0.45 | 0.46 | 0.47 |
| 15 | 0.20 | 0.22 | 0.24 | 0.26 | 0.28 | 0.30 | 0.32 | 0.33 | 0.34 | 0.36 | 0.36 | 0.37 | 0.38 | 0.39 |
| 16 | 0.17 | 0.18 | 0.20 | 0.22 | 0.23 | 0.25 | 0.26 | 0.27 | 0.28 | 0.28 | 0.29 | 0.30 | 0.31 | 0.32 |
| 17 | 0.13 | 0.14 | 0.15 | 0.16 | 0.18 | 0.19 | 0.20 | 0.20 | 0.21 | 0.21 | 0.22 | 0.23 | 0.23 | 0.24 |
| 18 | 0.09 | 0.10 | 0.10 | 0.11 | 0.12 | 0.13 | 0.13 | 0.14 | 0.14 | 0.14 | 0.15 | 0.15 | 0.15 | 0.16 |
| 19 | 0.05 | 0.05 | 0.05 | 0.06 | 0.06 | 0.06 | 0.07 | 0.07 | 0.07 | 0.07 | 0.08 | 0.08 | 0.08 | 0.08 |
| 17.5 | 0.11 | 0.12 | 0.12 | 0.14 | 0.15 | 0.16 | 0.16 | 0.17 | 0.17 | 0.18 | 0.18 | 0.19 | 0.19 | 0.20 |
| 15.56 (60°F.) | 0.18 | 0.20 | 0.22 | 0.24 | 0.26 | 0.28 | 0.29 | 0.30 | 0.30 | 0.32 | 0.33 | 0.33 | 0.34 | 0.34 |
| | *Add* | | | | | | | | | | | | | |
| 21 | 0.04 | 0.05 | 0.06 | 0.06 | 0.06 | 0.07 | 0.07 | 0.07 | 0.07 | 0.08 | 0.08 | 0.08 | 0.08 | 0.09 |
| 22 | 0.10 | 0.10 | 0.11 | 0.12 | 0.12 | 0.13 | 0.14 | 0.14 | 0.15 | 0.15 | 0.16 | 0.16 | 0.16 | 0.16 |
| 23 | 0.16 | 0.16 | 0.17 | 0.17 | 0.19 | 0.20 | 0.21 | 0.21 | 0.22 | 0.23 | 0.24 | 0.24 | 0.24 | 0.24 |
| 24 | 0.21 | 0.22 | 0.23 | 0.24 | 0.26 | 0.27 | 0.28 | 0.29 | 0.30 | 0.31 | 0.32 | 0.32 | 0.32 | 0.32 |
| 25 | 0.27 | 0.28 | 0.30 | 0.31 | 0.32 | 0.34 | 0.35 | 0.36 | 0.38 | 0.38 | 0.39 | 0.39 | 0.40 | 0.39 |
| 26 | 0.33 | 0.34 | 0.36 | 0.37 | 0.40 | 0.40 | 0.42 | 0.44 | 0.46 | 0.47 | 0.47 | 0.48 | 0.48 | 0.48 |
| 27 | 0.40 | 0.41 | 0.42 | 0.44 | 0.46 | 0.48 | 0.50 | 0.52 | 0.54 | 0.54 | 0.55 | 0.56 | 0.56 | 0.56 |
| 28 | 0.46 | 0.47 | 0.49 | 0.51 | 0.54 | 0.56 | 0.58 | 0.60 | 0.61 | 0.62 | 0.63 | 0.64 | 0.64 | 0.64 |
| 29 | 0.54 | 0.55 | 0.56 | 0.59 | 0.61 | 0.63 | 0.66 | 0.68 | 0.70 | 0.70 | 0.71 | 0.72 | 0.72 | 0.72 |
| 30 | 0.61 | 0.62 | 0.63 | 0.66 | 0.68 | 0.71 | 0.73 | 0.76 | 0.78 | 0.78 | 0.79 | 0.80 | 0.80 | 0.81 |
| 35 | 0.99 | 1.01 | 1.02 | 1.06 | 1.10 | 1.13 | 1.16 | 1.18 | 1.20 | 1.21 | 1.22 | 1.22 | 1.23 | 1.22 |
| 40 | 1.42 | 1.45 | 1.47 | 1.51 | 1.54 | 1.57 | 1.60 | 1.62 | 1.64 | 1.65 | 1.65 | 1.65 | 1.66 | 1.65 |
| 45 | 1.91 | 1.94 | 1.96 | 2.00 | 2.03 | 2.05 | 2.07 | 2.09 | 2.10 | 2.10 | 2.10 | 2.10 | 2.10 | 2.08 |
| 50 | 2.46 | 2.48 | 2.50 | 2.53 | 2.56 | 2.57 | 2.58 | 2.59 | 2.59 | 2.58 | 2.58 | 2.57 | 2.56 | 2.52 |
| 55 | 3.05 | 3.07 | 3.09 | 3.12 | 3.12 | 3.12 | 3.12 | 3.11 | 3.10 | 3.08 | 3.07 | 3.05 | 3.03 | 2.97 |
| 60 | 3.69 | 3.72 | 3.73 | 3.73 | 3.72 | 3.70 | 3.67 | 3.65 | 3.62 | 3.60 | 3.57 | 3.54 | 3.50 | 3.43 |
| 27.5 | 0.43 | 0.44 | 0.46 | 0.48 | 0.50 | 0.52 | 0.54 | 0.56 | 0.58 | 0.58 | 0.59 | 0.60 | 0.60 | 0.60 |

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* From the Assoc. Off. Agr. Chem., "Methods of Analysis" (1940).

† *Wiss. Abh. der Kaiserlichen Normal-Eichungs-Kommission,* **2,** 1900, pp. 140.

other than sucrose. However, the impurities other than sugar which are present in low-grade sugar products may cause an appreciable error in the Brix readings.

**Determination of Sucrose.** The main sugar of maple is sucrose. A small amount of invert sugar is normally present due to some hydrolysis of the sucrose. The sucrose may be determined readily in this mixture by a saccharimetric technique while the invert sugar is determined most readily by a gravimetric copper reduction method.

The saccharimeter reading on the normal weight of sample is due to the content of sucrose and invert sugar. The saccharimeter reading, based on a normal weight, after inversion of the sample, is due to the invert sugar originally present plus that derived from the hydrolysis of the sucrose. Use of these values in the proper formula permits the elimination of the effect of the invert sugar originally present and gives the percentage of sucrose present.

*Reagents.*

1. *Neutral lead acetate.* Prepare a saturated solution of neutral lead acetate.
2. *Hydrochloric acid solution.* Prepare 100 ml. of a hydrochloric acid solution with a specific gravity of 1.103 at 20° C.

*Saccharimeter Reading Before Inversion.* Rapidly weigh, to the nearest 0.005 gram, 52.00 grams of the sample (twice the normal weight) in a dish and transfer with water to a 200 ml. volumetric flask. Add 2–5 ml. of neutral lead acetate solution, dilute to volume and mix. Filter and discard the first 25 ml. of filtrate. Remove the excess lead from the filtrate by adding dry sodium carbonate, a little at a time, avoiding an excess; mix well and filter through a dry filter, discarding the first 25 ml. of filtrate. Pipette a 50 ml. aliquot of the lead-free filtrate into a 100 ml. volumetric flask, dilute to volume and mix thoroughly. Fill a 200 mm. saccharimeter tube with this solution and obtain a reading in the saccharimeter (see pp. 129–132). Twice the normal weight in a 200 ml. volume is equivalent to a normal weight in 100 ml. volume. A 50 ml. aliquot diluted to 100 ml. then represents a sample of one half the normal weight. Thus the saccharimeter reading obtained when multiplied by 2 will give the reading based on a normal weight. (Save the remainder of the solution for the gravimetric determination of the percentage of invert sugar.)

*Saccharimeter Reading After Inversion (Inversion at Room Temperature).* Pipette a 50 ml. aliquot of the filtrate from the original

200 ml. of clarified and deleaded solution into a 100 ml. volumetric flask. Add 10 ml. of the hydrochloric acid solution (specific gravity 1.103) and let stand for 24 hours at a temperature not below 20° C. If the temperature is above 25° C., a 10 hour digestion is sufficient. Dilute to volume and determine the saccharimeter reading at 20° C. employing a 200 ml. water jacketed saccharimeter tube to maintain a temperature of 20° C. (The large amount of fructose in the inverted sample necessitates accurate temperature control since the optical rotation of fructose changes appreciably with temperature.) Again, the 50 ml. aliquot represents one half the normal weight of sample and so the reading obtained, multiplied by 2, will give the saccharimeter reading based on a normal weight.

The sucrose present may then be calculated from the formula:

$$S = \frac{100\,(P - I)}{143.2 + 0.0676\,(m - 13) - t/2},$$

where

$S$ = percentage of sucrose;
$P$ = direct reading on a normal solution;
$I$ = invert reading on a normal solution;
$m$ = grams of total solids from the original sample in 100 ml. of the inverted solution;
$t$ = temperature at which the readings were made.

*Optional Rapid Inversion by Heating.* Pipette a 50 ml. aliquot of the filtrate from the original 200 ml. of clarified and de-leaded solution into a 100 ml. volumetric flask and add 25 ml. of water. Then, while rotating the flask, add, little by little, 10 ml. of the hydrochloric acid solution (specific gravity 1.103). Insert a thermometer in the flask and place the whole in a water bath held at 70° C. Agitate the contents of the flask constantly and heat until the thermometer in the flask reaches 67° C. Leave the flask in the bath exactly 5 min. longer, in which time the thermometer should reach approximately 69.5° C. Remove the flask and immediately place in a water bath at 20° C. When the contents of the flask have cooled to 35° C., rinse and remove the thermometer. Dilute almost to volume and leave the flask in a 20° C. bath for at least 30 min. Dilute to volume, fill a 200 mm. water-jacketed saccharimeter tube and obtain the reading on the saccharimeter. The result multiplied by 2 represents the reading after inversion based on a normal weight.

The sucrose present may be calculated from the formula:

$$S = \frac{100\,(P - I)}{143 + 0.0676\,(m - 13) - t/2}$$

where $S$, $P$, $I$, $m$, and $t$ have the same meaning as in the formula under inversion at room temperature.

**Determination of Invert Sugar.** Pipette 25.0 ml. of the solution used for obtaining the direct reading on the saccharimeter before inversion into a 400 ml. beaker. Add 25 ml. of water, 25 ml. of each of the two Fehling's solutions and determine the amount of cuprous oxide obtained by either the Munson and Walker or the Quisumbing and Thomas methods. Obtain the corresponding amount of invert sugar from the appropriate table. If the Munson and Walker method was used, obtain the values from the table headed "Invert sugar and sucrose, 2 grams of total sugar." (This is necessary to correct for the reducing action of the sucrose present in the sample.) Calculate the percentage of invert sugar present in the original syrup on the basis of the aliquot used and compare with the average value found in Table 20.

**Adulteration with Other Sugars.** The most common adulterants of maple syrup are sucrose and brown sugar. Since the sugar of maple syrup is mainly sucrose, the detection of the above adulterants is based upon constituents present in these products other than the sugars, e.g., ash, type of ash, and organic matter precipitated with lead.

The adulteration of maple syrup with glucose or invert sugar may be determined readily by the great increase in reducing sugar present or by the marked change in saccharimetric readings from the normal for maple syrup. Consequently, these sugars are not used to any extent for the adulteration of maple syrup.

A study of the minor constituents of maple syrup, e.g., ash and organic matter will show if sucrose or brown sugar is present. Maple syrup contains mineral matter originally contained in the maple sap. Pure sucrose has been refined so that it contains practically no ash. The adulteration of maple syrup with sucrose will cause a reduction in the ash content of the syrup. Impure sugars, such as brown sugar, contain minerals and so have an appreciable ash content. The adulteration of maple syrup with brown sugars cannot be detected then by the change in total ash content. However the nature of the ash in brown sugar is quite different from that of maple syrup. This difference in the nature of the ash results in differences in solubility and alkalinity of the ash from the two sources. These differences are used for detecting brown sugar as an adulterant.

Maple syrup contains certain soluble organic substances (organic acids, salts of organic acids, soluble proteins, etc.) which will precipitate with lead acetate, whereas pure sucrose solutions do not. The determination of the volume or weight of precipitate obtained by treating a sample of syrup with lead acetate may then be used as a criterion of its adulteration with pure sucrose. The Sy method is a rapid method for determining the volume of lead precipitate, whereas the more accurate Winton lead number determines gravimetrically the amount of lead precipitated.

**Determination of Total Ash.** Carefully char a 5 gram sample of the syrup contained in a crucible or dish over a burner. Caution is required in preventing the syrup from boiling over in the heating process, and a wide-mouthed platinum crucible or dish is advantageous. Place in a muffle furnace at 525° C. and ash until free from carbon. (Maple ash may have a greenish purple appearance due to the presence of manganese.) Remove the dish from the muffle furnace, cool, and moisten the ash with 1 ml. of water. Evaporate on the steam bath, then heat to dryness on a hot plate or over a burner and return to the muffle furnace at 525° C., heating until constant weight is obtained. If the presence of brown or impure sugar is suspected, save the ash for the determination of its solubility and alkalinity. Calculate the percentage of total ash present in the sample and compare with the average value given in Table 20.

**Solubility of the Ash.** Add water to the ash and heat almost to boiling. Filter through a quantitative ashless filter paper and wash with hot water until the total volume of filtrate and washings measures approximately 60 ml. (Save the filtrate for the determination of the alkalinity of the soluble ash.) Return the filter and its contents to the crucible and re-ignite it in the muffle furnace to constant weight at 525° C. The weight of ash remaining represents the amount of insoluble ash, and the difference in weight from the total ash represents the amount of soluble ash. Calculate the percentage of soluble and insoluble ash present in the sample. Also, calculate the ratio of the soluble to the insoluble ash present and compare with the values given in Table 20.

**Alkalinity of the Soluble Ash.** Titrate the cool filtrate and washings containing the soluble ash (obtained previously in determining percentage of soluble and insoluble ash) with standard 0.1 N hydrochloric acid solution using methyl orange indicator.

Calculate the alkalinity in terms of milliliters of 1 N acid per 100 grams of original syrup sample.

**Alkalinity of the Insoluble Ash.** From a burette, add an excess of standard 0.1 N hydrochloric acid solution to the dish containing the insoluble ash. This usually requires 10–15 ml. of the acid. Heat almost to boiling on an asbestos plate or gauze and cool. Titrate the excess standard acid with standard 0.1 N sodium hydroxide solution using methyl orange indicator. Calculate the alkalinity of the ash in terms of milliliters of 1 N acid per 100 grams of original sample. Also, calculate the ratio of the alkalinity of the soluble to the alkalinity of the insoluble ash and compare with the values given in Table 20.

**Sy Lead Number.**[1] This is a simple rapid method for determining the volume of precipitate obtained when lead acetate is added to a syrup sample. This method is not as accurate as the more complicated gravimetric determinations of the weight of lead precipitated.

In this method a measured amount of syrup is treated with a definite amount of lead acetate solution and the volume of precipitate obtained is measured after standing for 20 hours. The comparison of the volume of precipitate with the average volume obtained on pure maple syrups will give an approximation of the percentage purity of the sample.

*Reagent.*

1. *Basic lead acetate solution:* To 430 grams of normal lead acetate and 130 grams of litharge, add 1 liter of water and boil for 30 min. Cool and allow the insoluble matter to settle. Decant off the supernatant liquid and dilute it to a specific gravity of 1.25 with recently boiled distilled water.

*Procedure.* Measure 5 ml. of the syrup sample into a 25 ml. cylinder graduated into fifths of a milliliter. Make up to the 15 ml. mark with water and add 2 ml. of the basic lead acetate solution. Thoroughly mix by shaking and let stand for 20 hours. Read the volume of precipitate. Pure maple syrup should give at least 3 ml. of precipitate and usually over 5 ml.

**Winton Lead Number.** A weighed sample is treated with a measured excess of standard lead acetate solution and the excess lead acetate determined gravimetrically. By difference, the amount of lead acetate reacting with the organic matter in the syrup is determined. From this the per cent of lead precipitated by the sample is calculated as the lead number.

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[1] Sy, *J. Amer. Chem. Soc.*, 30, 1430 (1908).

*Reagent.*

1. *Basic lead acetate solution.* Prepare activated litharge by heating it at 650°–670° C. for 2.5–3 hours in a muffle furnace. When cool, the product should have a lemon color. Boil 80 grams of normal lead acetate crystals and 40 grams of the freshly activated litharge with 250 grams of water for 45 min. in a 500 ml. Erlenmeyer flask equipped with a reflux condenser. After cooling, filter off any residue and dilute with recently boiled distilled water to a density of 1.25 at 20° C. Dilute a measured volume of this prepared stock solution with 4 volumes of water and filter.

*Blank Determination.* A blank determination must be run with each set of samples to determine the concentration of the lead solution used. Pipette 25.00 ml. of the lead acetate solution into a 100 ml. volumetric flask, add a few drops of glacial acetic acid to clarify the solution, and dilute to volume with distilled water. The solution must be clear to insure that all the lead is in solution. Shake the solution and let stand 3 hours or more before filtering. Pipette 10.00 ml. of the clear filtrate into a 250 ml. beaker, add 40 ml. of distilled water, 1 ml. of concentrated sulfuric acid, stir, and add 100 ml. of ethyl alcohol. Cover the beaker with a watch glass and let stand over night. Filter on a previously prepared and weighed Gooch crucible, wash with ethyl alcohol, and dry at 100° C. in an oven. Ignite in a muffle furnace, cool, and weigh to determine the amount of lead sulfate obtained.

*Sample Determination.* Weigh 25.00 grams of the syrup sample in a dish and transfer with water to a 100 ml. volumetric flask. Pipette 25.00 ml. of the standard lead acetate solution into the flask and shake. Dilute to volume with distilled water and continue the determination as in the blank determination. Subtract the weight of lead sulfate found for the sample from the weight of lead sulfate found for the blank to obtain the weight of lead sulfate corresponding to the amount of lead precipitated by the sample. Multiply the difference by the gravimetric factor 0.6833 ($Pb \div PbSO_4$), divide by the weight of sample represented in the aliquot, and multiply by 100 to obtain the lead number. If an exactly 25.00 gram sample is used, simply multiply the difference by 27.33 to obtain the lead number. Compare with the average value given in Table 20.

# CHAPTER XV

# SOILS

Soil is that portion of the earth's surface consisting of disintegrated and more or less decomposed rock material, which, acted upon by organic agencies and mixed with varying quantities of organic matter, may provide conditions necessary for the growth of plants. Of the various soil components, some are in a form readily available for use by a plant while others are not. Varying quantities of numerous groups of microorganisms live in the soil and, for some groups, their activity is reflected in changes in the availability of soil components.

Thus, analyses may be made on a soil to determine the amounts of the elements present (ultimate analysis), the amounts potentially available or readily available for plant food, the amounts and kinds of microorganisms present, and certain physical chemical characteristics. Of these, only the ultimate analysis and the physical chemical procedure for *p*H will be considered in this book.

**Collection and Preparation of the Sample.** Scrape off all surface accumulation of decaying grass, leaves, and other foreign matter and, by means of a soil auger, remove a core of soil from the surface to the desired depth, depending upon the purpose for which the analyses are to be used. To obtain a representative sample of soil from a plot, secure a number of such cores of soil, depending upon the size of the plot, taken at definite spaced intervals throughout the plot and mix into a composite sample.

Remove all stones from the composite soil sample, shake out roots and foreign matter, and expose the soil in a thin layer in a warm room until it is air-dry. After drying, pulverize the lumps and mix the soil thoroughly on a paper or cloth. Mix and quarter according to the procedure described on page 18 until a sample of the proper size is obtained.

Pulverize the air-dry soil in a porcelain mortar to pass through a 40-mesh sieve, taking care not to crush the rock fragments. Discard the material that does not pass through the sieve. Thoroughly mix the sifted soil and place in a tightly closed container.

**Determination of Moisture.** Weigh accurately a sample of approximately 2 grams of the sifted soil into an aluminum moisture dish and dry for 5 hours at 105° C. in a drying oven. From the loss in weight on drying, calculate the percentage of moisture present in the air-dry soil.

**Determination of Loss on Ignition.** Carefully transfer the dried soil from the moisture determination to a platinum dish. Ignite to full redness until all the organic matter is destroyed. Cool in a desiccator and weigh. Calculate the loss in weight as loss on ignition. (This method only approximates the organic matter present, especially for those soils containing appreciable quantities of combined water.)

## ULTIMATE ANALYSIS OF A SOIL

**Preparation of the Sample.** Grind the soil, previously passed through the 40-mesh sieve, in a procelain mortar to pass through an 80–100-mesh sieve. Thoroughly mix the sifted soil and place in a tightly closed container.

**Sodium Carbonate Fusion.** This prepares the sample for the determination of silica, iron, aluminum, titanium, calcium, magnesium and manganese.

*Procedure.* Introduce 5 grams of anhydrous sodium carbonate into a 30 ml. platinum crucible. Place an accurately weighed 1 gram sample of soil on top of the sodium carbonate and mix thoroughly with the sodium carbonate using a glass rod. Level off the mixture and brush into the crucible any particles adhering to the glass rod. Layer approximately 0.5 gram of sodium carbonate upon the mixture.

Set the crucible in a slightly inclined position on a platinum or nichrome triangle. Place the lid on the crucible so that it is about one fourth open to prevent reducing conditions. Heat *slowly* to dull redness to avoid spattering, then *gradually* increase the heat to a good flame of a Meker burner. Insure that reducing conditions do not develop by keeping the crucible partly open and not permitting the burner flames to envelope the opening. After 10–15 min. of intense heating, gas bubbles should no longer come off, indicating that the fusion is complete. If patches of fused material stick to the sides of the crucible, heat these places intensely to make the material accumulate into one mass, and leave the sides of the crucible clean. This will aid in the removal of the fused mass later. To insure complete oxidation, remove the lid and heat the crucible 1–2 min. Remove the flame, cool momentarily, pick up the crucible with the tongs and give it a rotary motion so that the contents are spread over the sides of the lower one third of the crucible. This, also, will aid in the removal of the fused mass later. Allow the crucible and contents to cool.

**Determination of Silica.** Silica ($SiO_2$) is separated by dehydration in acid solution and filtration from the other components of the soil. Upon ignition, the weight of impure silica is obtained. Treatment with hydrofluoric and sulfuric acids volatilizes the silica and the residue remaining is weighed. The difference in weights, before and after treatment with hydrofluoric and sulfuric acids, gives the weight of silica present in the sample.

*Reagents.*

1. *An approximately 5 N hydrochloric acid solution* prepared by adding 200 ml. of the concentrated acid to water and diluting to 500 ml.
2. *An approximately 2.2 per cent hydrochloric acid solution* prepared by adding 5 ml. of concentrated hydrochloric acid to 95 ml. of water.

*Procedure.* Half fill the crucible containing the sodium carbonate fusion with water. Heat the crucible gently, without causing it to boil, by moving the flame around the sides of the crucible. If the crucible is clean and in good condition and the fusion properly made, the fused cake will break away from the sides of the crucible and may be transferred to a casserole. Wash the crucible and lid with a little water using a stirring rod equipped with a rubber policeman and a few drops of hydrochloric acid if some of the fused material perists in remaining. Place a watch glass on the casserole and add 75 ml. of 5 N hydrochloric acid through its lip. (If the fused cake does not break away from the sides of the crucible, so that it cannot be transferred to the casserole, place the crucible and cover in the casserole and dissolve the fused contents with the 75 ml. of 5 N hydrochloric acid solution.)

Heat the covered casserole containing the fused cake and hydrochloric acid on the steam bath to aid the decomposition of the material. When the evolution of carbon dioxide stops, remove the watch glass and wash it off into the casserole. Evaporate the contents until the residue begins to crumble and powder; do not evaporate further. The evaporation, especially near the end, is aided by breaking up the lumps.

Add 15 ml. of the 5 N hydrochloric acid solution to the residue, cover with a watch glass and digest on the steam bath for approximately 10 min. or until all the iron is in solution, as evidenced by the absence of brown specks. Add 10 ml. of water, stir thoroughly, and filter. Wash with the hot 2.2 per cent hydrochloric acid solution until all salts are removed (approximately fifteen washings are required).

Some silica always remains in solution after the first filtration. To recover this, evaporate the filtrate and washings again in the same casserole until the odor of acid practically disappears. Heat in a 100° C. oven for 2 hours, then add 10 ml. of 5 N hydrochloric acid solution and filter immediately. Wash ten times with a cold solution containing 1 ml. of concentrated hydrochloric acid per 99 ml. of water. Save the filtrate and washings for the ammonia separation of the $R_2O_3$ group.

Transfer the paper and contents from this second filtration to a platinum crucible and ignite *gently* until all the carbon has been burned. Add to the crucible and contents the filter containing the silica from the first filtration and ignite again. Do not burn the filter rapidly or mechanical loss of silica will occur. With the crucible nearly covered, heat with a Meker burner to constant weight. A 20-min. heating is usually sufficient, especially if lumps have been previously broken up with a platinum rod.

Add 2–3 ml. of water to the impure silica in the crucible, followed by 5 drops of concentrated sulfuric acid. Slowly add about 5 ml. of hydrofluoric acid and evaporate to approximate dryness on a sand bath heated by a hot plate. After cooling, add 1–2 ml. of hydrofluoric acid and rotate the crucible in an inclined position to dissolve any silica which may stick to the sides. Evaporate to dryness on the sand bath, then ignite gently until the fumes from the sulfuric acid cease to come off. Continue the ignition of the crucible to bright redness and finish by heating with a Meker burner for a few minutes. After cooling, weigh the crucible and contents. (Save the crucible and contents for the ammonia separation of the remaining elements.) The difference between the weight of crucible and contents before and after treatment with sulfuric and hydrofluoric acids represents the weight of pure silica. Calculate and report the percentage of silica in the sample.

*Remarks.* When dehydrating the silica from the hydrochloric acid treatment of the fusion, never allow the temperature to go above 110° C. or erroneous results will be obtained. It is impossible to recover all the silica in one dehydration since dehydrated silica is somewhat soluble in hydrochloric acid, depending upon the concentration and volume of acid and the time of contact. The conditions of the second dehydration minimize the loss of silica as much as possible. Great care should be exercised in igniting the silica. The filter paper should be ignited slowly, with low heat, and should never be allowed to flame. An intense heat may cause the formation of silicon carbide. Consequently, the ignition to constant weight is conducted with low to moderate heat.

**The Ammonia Separation of Iron, Aluminum, Titanium, and Phosphorus from Manganese, Calcium and Magnesium.** This separation depends upon the insolubility of the hydroxides and phosphates of iron, titanium, and aluminum at, or near, the neutral point and the solubility of the hydroxides of calcium, manganese and magnesium at this *p*H, especially in the presence of ammonium chloride.

*Reagents.*

1. *An approximately 5 N solution of hydrochloric acid* (see p. 249).
2. *An approximately 5 N solution of ammonium hydroxide* prepared by diluting 340 ml. of concentrated ammonium hydroxide to a volume of 1 liter with water.
3. *An approximately 1 N solution of ammonium hydroxide* prepared by diluting 100 ml. of the 5 N solution to a volume of 500 ml.
4. *An approximately 0.5 per cent solution of ammonium chloride, adjusted to a pH of 6.2,* prepared as follows: To approximately 800 ml. of water, add 7.6 ml. of concentrated hydrochloric acid, sufficient bromocresol purple indicator solution, and 5 N ammonium hydroxide solution until the solution just changes from a yellow to a purple color. Dilute to a total volume of 1 liter with water. The solution must be maintained at a *p*H of 6.2; if the solution turns yellow upon heating, add a few drops of the 5 N ammonium hydroxide solution until the purple color is restored.
5. *Bromocresol purple indicator solution* (see p. 71).
6. *Thymol blue indicator solution* (see p. 72).

*Procedure.* Fuse the residue in the crucible from the silica determination with 1 gram of sodium carbonate. Dissolve with a small volume of 5 N hydrochloric acid solution and combine with the filtrate and washings from the silica determination in a 600 ml. beaker. Evaporate the volume of the combined solutions to 300 ml.

Add 5 ml. of concentrated hydrochloric acid, 1 ml. of glacial acetic acid, 3 drops of thymol blue indicator solution and sufficient 5 N ammonium hydroxide solution to turn the solution just yellow (at approximate *p*H 2.5). Heat, boil for one-half minute, and place a strip of lacmoid paper into the solution on the side of the beaker. Immediately add the 1 N ammonium hydroxide solution from a burette until a *p*H of 6.2 is reached. This is accomplished by adding the ammonium hydroxide solution rapidly at first, with vigorous stirring, until a precipitate starts to form, then more slowly until the paper just turns blue. Add the 1 N ammonium hydroxide, drop by drop, until the solution produces a distinct purple color when added to a fraction of a drop of bromocresol purple indicator on a spot plate. Add 3 additional drops of the 1 N ammonium hydroxide solution. (This neutralization process should be accomplished as rapidly as possible.) *Immediately heat and boil not longer than a few seconds.* Filter immediately, keeping the solution hot over a low flame. Wash with the hot 0.5 per cent ammonium chloride solution, adjusted to a *p*H of 6.2.

To remove traces of calcium, manganese, and magnesium carried down in the precipitate, redissolve the precipitate in approximately 20 ml. of hot 5 N hydrochloric acid solution. Add 7 drops of glacial acetic acid, reprecipitate and wash as previously described, but do not add any additional hydrochloric acid over that required to dissolve the precipitate. (Save the combined filtrates for subsequent analyses.)

Transfer the filter containing the washed precipitate into a weighed platinum crucible and ignite. Complete the ignition to constant weight by heating with a Meker burner for 5–10 min. Insure the maintenance of good oxidizing conditions throughout the ignition. The crucible, after ignition, should contain the oxides of aluminum, iron, titanium, and phosphorus. Calculate percentage of total combined oxides in the sample.

*Remarks.* In very rare instances, soils may be encountered with insufficient iron, aluminum, and titanium to combine with all the phosphorus. In these instances, known quantities of iron are added, and a correction made later for the added iron.

**Determination of Iron and Titanium.** The oxides of aluminum, iron, phosphorus, and titanium are fused with potassium bisulfate and dissolved in acid. The iron and titanium are reduced by passing the solution through a Jones reductor and titrated with a standard potassium permanganate solution. The titration figure represents the reducing action of both the iron and titanium. The percentage of titanium is determined independently by a colorimetric procedure. Subtracting the reducing effect of the titanium from the titration of the iron and titanium permits the calculation of the amount of iron present.

*Reagents.*

1. *An approximately 2 N solution of sulfuric acid* prepared by diluting 57 ml. of concentrated sulfuric acid to one liter of solution with water.
2. *A standard 0.1 N potassium permanganate solution.*
3. *An approximately 10 per cent by volume sulfuric acid solution* prepared by diluting 10 ml. of concentrated sulfuric acid to 100 ml. of solution with water.
4. *A standard titanium solution* prepared as follows: Grind together exactly 0.1000 gram of titanium oxide with 2 grams of potassium bisulfate and fuse in a platinum crucible. Heat just high enough to start a moderate evolution of sulfur trioxide fumes but take care to heat until all the titanium oxide is in solution. Fill the crucible two-thirds full with 2 N sulfuric acid solution and warm gently to dissolve the fused mass. Transfer to a 100 ml. volumetric flask and dilute to volume with the 2 N sulfuric acid. Transfer a 5.00 ml. aliquot of this solution to a 100 ml. volumetric flask, add approximately 90 ml. of the 2 N sulfuric acid, 2 ml. of a 3 per cent hydrogen peroxide solution, dilute to volume with the 2 N sulfuric acid solution and mix thoroughly.

*Procedure* Add 5 grams of potassium bisulfate to the crucible containing the ignited precipitate from the ammonia separation and carefully fuse until the oxides are in solution as evidenced by the absence of solid brown particles in the liquid fusion. The fusion should be conducted *in the hood over a low flame* just sufficient to heat the bottom of the crucible to a faint redness and cause a moderate evolution of sulfur trioxide fumes until the fusion is complete. The fusion should not be continued longer than necessary since the crucible is attacked to some extent.

Transfer the crucible and contents to a 400 ml. beaker, add sufficient 10 per cent by volume sulfuric acid solution and digest on the steam bath until the cake is dissolved. Wash the crucible with the sulfuric acid solution and remove it from the beaker. Dilute to a total volume of approximately 100 ml. with the 10 per cent by volume sulfuric acid solution, pass the solution through a Jones reductor (see p. 91), and immediately titrate with the standard 0.1 N potassium permanganate solution. The volume of permanganate solution required represents the reducing action of both the iron and titanium present in the sample.

Should any white particles of silica be observed, filter the solution, dry, and weigh the solid matter obtained and add this weight of silica to that previously obtained.

The titrated solution containing iron and titanium is now evaporated to approximately 50 ml., filtered if cloudy, cooled, and sufficient 3 per cent hydrogen peroxide solution added to fully peroxidize the titanium (usually 2–4 ml. of 3 per cent hydrogen peroxide solution is required). Thoroughly mix the solution, transfer to a volumetric flask (100 ml. or larger, depending upon the color intensity) and dilute to the mark.

Compare the color of the solution with a standard titanium solution using a suitable colorimeter and calculate the percentage of titanium oxide ($TiO_2$) found in the sample.

Calculate the equivalence of the $TiO_2$ in terms of milliliters of the standard 0.1 N potassium permanganate solution and subtract from the volume of the permanganate solution used for the titration of the iron and titanium to obtain the volume of standard permanganate solution equivalent to the iron present. Calculate the percentage of iron oxide ($Fe_2O_3$) present in the sample.

*Remarks.* A necessary precaution to observe is that no hydrofluoric acid is present or comes into contact with the determination while it is being conducted or the color will be bleached.

The color comparison between the standard and unknown titanium solutions may be made in cylinders instead of a colorimeter. Add 25 or 50 ml. of the unknown solution to a comparison cylinder. Add measured volumes of the standard color solution to another comparison cylinder until the colors in the two cylinders match, holding both cylinders over a piece of white paper in a good light.

**Determination of Calcium.** The calcium is precipitated as the oxalate, filtered, washed, dissolved and titrated with a standard potassium permanganate solution The amount of calcium present is calculated from the volume of standard potassium permanganate solution required.

*Reagents.*

1. *A hydrochloric acid solution (1:9)* prepared by adding 1 volume of concentrated hydrochloric acid to 9 volumes of water.
2. *A sulfuric acid solution (1:4)* prepared by adding 1 volume of concentrated sulfuric acid to 4 volumes of water.
3. *An ammonium hydroxide solution (1:1)* prepared by diluting 1 volume of concentrated ammonium hydroxide with 1 volume of water.

4. *A standard 0.1 N potassium permanganate solution.*
5. *A saturated ammonium oxalate solution* prepared by saturating 100 ml. of water with ammonium oxalate.

*Procedure.* Concentrate the combined filtrates and washings from the ammonia separation to a volume of approximately 50 ml. Make the solution slightly alkaline with an ammonium hydroxide solution (1:1). Then, while still hot, add a saturated ammonium oxalate solution, drop by drop, until complete precipitation occurs, and add several milliliters more to insure an excess. Heat the solution to boiling and let stand for 3 hours or longer.

Decant the supernatant liquid through a filter and wash the precipitate in the beaker with 15–20 ml. of hot water. Let stand until the precipitate settles out and again decant the supernatant liquid through the same filter. Dissolve any precipitate on the filter with hot hydrochloric acid solution (1:9), collecting the washings in the original beaker. Wash the filter six times with hot water. Heat the filtrate and washings to boiling and reprecipitate the calcium by the addition of the ammonium hydroxide solution and a little ammonium oxalate solution. Let stand as in the previous situation, filter through the same filter, and wash free from oxalates with hot water. (Save the filtrates and washings from both precipitations for the determination of manganese and magnesium.)

Make a hole in the bottom of the filter and wash the calcium oxalate precipitate into the beaker used for precipitation. Thoroughly wash the filter with hot sulfuric acid solution (1:4) and titrate the solution, while hot (85°–90° C.), with the standard 0.1 N potassium permanganate solution. Calculate the percentage of calcium present in the sample.

**Determination of Manganese and Magnesium.** The manganese and magnesium are precipitated by the addition of sodium ammonium hydrogen phosphate solution, filtered off and washed. The precipitate is dissolved in a measured volume of standard sulfuric acid solution and the excess acid titrated with a standard sodium hydroxide solution. The titration represents the phosphates combined with the manganese and magnesium. The manganese is then determined independently by the bismuthate method and the magnesium calculated by difference.

*Reagents.*

1. *An approximately 0.5 N ammonium hydroxide solution* prepared by dissolving 34 ml. of concentrated ammonium hydroxide in water and diluting to a volume of 1000 ml.

2. *A 10 per cent sodium ammonium hydrogen phosphate solution* prepared by dissolving 10 grams of the salt in 90 grams of water.
3. *A 1 per cent sodium oxalate solution* prepared by dissolving 1 gram of the salt in 99 grams of water.
4. *Bromocresol green indicator solution* prepared by grinding together in a mortar 0.1 gram of the dry indicator with 14.3 ml. of 0.01 N sodium hydroxide solution and diluting with water to a volume of 250 ml.
5. *A standard 0.1 N sulfuric acid solution.*
6. *A standard 0.1 N sodium hydroxide solution.*
7. *A standard 0.1 N ferrous sulfate solution.*
8. *A standard 0.1 N potassium permanganate solution.*

*Procedure.* The filtrates and washings from the calcium determination are evaporated to dryness with 5 ml. of concentrated nitric acid to remove excess ammonium salts. Add 5 ml. of concentrated hydrochloric acid to the residue, dilute to 100 ml. and neutralize with ammonium hydroxide solution. Add 20 ml. of the 10 per cent sodium ammonium hydrogen phosphate solution, then 10 ml. of concentrated ammonium hydroxide solution. Bring the solution to a boil and let stand at room temperature over night.

Filter off the precipitate and wash with the 0.5 N ammonium hydroxide solution. Dry the filter paper and contents in the air until free from ammonia. Transfer the filter and contents to a 300 ml. Erlenmeyer flask, add 50 ml. of carbon dioxide-free water (recently boiled and cooled), and add a measured volume of the standard 0.1 N sulfuric acid solution in excess of that required for solution. Vigorously shake the contents of the flask to disintegrate the paper and back-titrate the excess standard acid with the standard 0.1 N sodium hydroxide solution to a $p$H of 4.5, using bromocresol green as indicator. The titration indicates the amount of phosphate combined with manganese and magnesium.

The reactions involved in the titration are:

$$MgNH_4PO_4 + H_2SO_4 \rightarrow MgSO_4 + NH_4H_2PO_4$$
$$MnNH_4PO_4 + H_2SO_4 \rightarrow MnSO_4 + NH_4H_2PO_4.$$

*Procedure for Determining Manganese by the Bismuthate Method.* Add approximately 12 ml. of concentrated nitric acid to the solution after titration of the combined phosphates of magnesium and manganese. Filter the solution and wash the filter with water. Evaporate the filtrate and washings on the steam bath to a volume of approximately 50 ml. Cool the solution to room temperature, add 0.5 gram of sodium bismuthate, stir, and allow to stand 15–30 min. Filter through a Gooch crucible prepared with an asbestos mat which has been ignited, treated with a 4 per cent potassium permanagnate solution, and washed with water. Wash the residue with a 3 per cent nitric acid solution until no further color is obtained in the washings.

To the filtrate and washings, add a measured volume of standard 0.1 N ferrous sulfate solution in excess and immediately titrate with standard 0.1 N potassium permanganate solution to the end point.

Conduct a blank determination, using all the reagents, adding the same volume of standard 0.1 N ferrous sulfate solution used in the sample and titrate to the end point with the standard 0.1 N potassium permanganate solution.

From the difference in titration values of the blank and sample, calculate the amount of manganese present in the sample.

*Calculations.* Calculate the percentages of MgO and MnO with the aid of the following formulas:

$$(1) \qquad \frac{\text{g. Mn found} \times 1.2913 \times 100}{\text{Sample weight}} = \%\ \text{MnO},$$

where 1.2913 is the chemical factor $\left(\frac{\text{MnO}}{\text{Mn}}\right)$.

$$(2) \quad \left(T_{\text{ml.}} \times \text{n.f.} - \frac{\text{g. Mn found} \times 3.0575}{0.08398}\right) \times \frac{0.02016 \times 100}{\text{Sample weight}} = \%\ \text{MgO},$$

where

$T_{\text{ml.}}$ = titration in milliliters of standard 0.1 N sulfuric acid solution required for the combined magnesium and manganese phosphates;

n.f. = normal factor of the standard 0.1 N sulfuric acid solution;

3.0575 = chemical factor $\left(\frac{\text{MnNH}_4\text{PO}_4}{\text{Mn}}\right)$;

0.08398 = milliequivalent weight of $MnNH_4PO_4$;

0.02016 = milliequivalent weight of MgO.

**Determination of Phosphorus.** The organic matter is burned off, the phosphorus put into solution, precipitated as ammonium phosphomolybdate, filtered, and washed. The precipitate is dissolved in a measured volume of standard sodium hydroxide solution, the excess alkali back-titrated with a standard acid solution, and the amount of phosphorus calculated.

*Reagents.*

1. *Ammonium molybdate solution* (see p. 267).
2. *Ammonium nitrate solution* (*2.5 per cent*) prepared by dissolving 2.5 grams of ammonium nitrate in 97.5 grams of water.
3. *Standard 0.1 N sodium hydroxide and nitric acid solutions.*
4. *Magnesium nitrate solution* (see p. 265).

*Procedure.* Weigh accurately a sample of approximately 5 grams of soil (80–100 mesh) into a porcelain dish. Moisten the soil with 5–7 ml. of the magnesium nitrate solution, dry on a steam bath and burn off the organic matter at low redness. Allow to cool and add 10 ml. of water, 10 ml. of concentrated hydrochloric acid, and 5 ml. of concentrated nitric acid. Cover the dish with a watch glass and digest for 2 hours on the steam bath, stirring a few times during the digestion.

Transfer the contents of the dish to a 250 ml. volumetric flask and dilute to volume with water. Mix thoroughly and filter through a dry filter, pouring the first portions of the filtrate back through the filter until the filtrate is clear.

Transfer an aliquot of the solution representing 4 grams of soil to a glass beaker or porcelain dish and evaporate to dryness on the steam bath. Take up with a nitric acid solution (1:4), evaporate to dryness, and heat for 1 hour at 110°–120° C. Again take up with the 1:4 nitric acid solution, filter to remove small amounts of silica and wash with the nitric acid solution collecting the liquid in a beaker. Reduce the combined volume of filtrate and washings to 30–40 ml. Make the solution alkaline with ammonium hydroxide solution (1:1) and dissolve the precipitate with the nitric acid solution (1:4), using a slight excess. Add 5 grams of ammonium nitrate crystals and with vigorous stirring slowly add 15 ml. of the ammonium molybdate solution. Maintain the solution at 45° C. for 1 hour, then let stand at room temperature over night.

Filter, wash thoroughly with the 2.5 per cent ammonium nitrate solution and then with cold water. Transfer the filter and contents to the beaker in which the precipitation occurred. Add standard 0.1 N sodium hydroxide solution from a burette until the precipitate is dissolved and the solution alkaline, using phenolphthalein as indicator. An excess of sodium hydroxide is required to completely dissolve the yellow precipitate. Back-titrate the excess alkali with standard 0.1 N nitric acid solution and calculate the percentage of phosphorus as $P_2O_5$, present in the soil.

**Determination of Aluminum.** This percentage is calculated from the results of the preceding determinations. The sum of the percentages of $Fe_2O_3$, $P_2O_5$, and $TiO_2$ subtracted from the total percentage of oxides of iron, titanium, aluminum and phosphorus obtained in the ammonia separation gives the percentage of $Al_2O_3$.

**Determination of Potassium and Sodium.** Upon fusing the soil with a mixture of ammonium chloride and calcium carbonate, the sodium and potassium are converted to soluble chlorides with practically only calcium and magnesium as other soluble components. The latter are removed by precipitating them as the practically insoluble carbonates and filtering. Sodium and potassium are weighed as combined chlorides. Further treatment with platinic chloride forms the sodium and potassium chloroplatinates. The potassium chloroplatinate is insoluble in approximately 87 per cent alcohol and is removed from the soluble sodium chloroplatinate, dried, and weighed. Calculating the potassium found as potassium chloride and subtracting this weight from the combined weight of the chlorides gives the weight of sodium chloride. The amounts of sodium and potassium found are then used to calculate the percentages of sodium and potassium oxides in the soil.

*Reagents.*

1. *Ammonium carbonate solution* prepared by saturating a volume of water with the salt.
2. *Ammonium chloride solution* prepared by dissolving 100 grams of the salt in 500 ml. of water and saturating with potassium chloroplatinate (see p. 272).
3. *Acidulated alcohol—2.25 N solution* prepared by passing HCl gas into a mixture of 2000 ml. of 95 per cent ethyl alcohol and 152 ml. of concentrated hydrochloric acid.
4. *An approximately 87.5 per cent by weight ethyl alcohol solution* prepared by adding 32 ml. of water to 669 ml. of 95 per cent ethyl alcohol.
5. *A 10 per cent platinic chloride solution* prepared by dissolving 1 gram of the salt in 9 grams of water.

*Procedure.* Mix 1.000 gram of the soil sample with 1 gram of dry ammonium chloride in an agate mortar. Add 8 grams of calcium carbonate and mix thoroughly. Place a small amount of sodium carbonate in a platinum crucible and then transfer the mixture from the mortar to the crucible. Rinse the mortar with a little calcium carbonate and add to the crucible. Set the crucible in a hole in an asbestos board so that about one fourth of the crucible projects above the surface of the board. Heat the crucible slowly until fumes from the ammonium salts are no longer visible and the lower portion of the crucible is dull red, then maintain this temperature for 40–60 min. The fused mass does not become liquid but contracts in volume because the fused calcium chloride is absorbed by the great quantity of calcium carbonate present. Too high a temperature is avoided to prevent volatilization of the sodium and potassium chlorides and also to prevent fusion of the silicates or the mass cannot be disintegrated in water.

Transfer the contents of the crucible to a porcelain casserole covered with a watch glass, using a glass rod to aid in the removal of the fused mass from the crucible. Add water to the crucible and digest until all the remaining matter can be washed out into the casserole or until it is thoroughly extracted. (If the cake is not readily removed from the crucible, place the crucible and contents in the casserole.) Slake with water and disintegrate the lumps with an agate pestle. Digest on the steam bath to aid the disintegration of the mass. Filter by decantation, washing the solid material in the casserole five times with hot water before transferring it to the filter. Wash the filter and contents with 300 ml. of hot water.

Add ammonium carbonate solution to the filtrate to precipitate the calcium and any magnesium present. Allow to settle, decant the supernatant liquid into a porcelain dish and concentrate by evaporation, finally transferring the precipitate to the dish. Reduce the volume to approximately 30 ml., add a little ammonium carbonate solution and ammonium hydroxide and heat to boiling. Filter into a porcelain dish, evaporate the filtrate to dryness on the steam bath and expel the ammonium salts by ignition at a low temperature just sufficient to drive off ammonium chloride fumes. Dissolve the residue in 5 ml. of water. Add a few crystals of ammonium oxalate and a few drops of ammonium hydroxide to remove the last of the calcium, warm and filter through a small filter into a previously weighed platinum dish. Evaporate to dryness on a steam bath. Carefully heat the residue to incipient fusion, cool and weigh as sodium and potassium chlorides.

Dissolve the combined chlorides in 30 ml. of water, add 1.5 ml.

of the platinic chloride solution and evaporate to a sirupy consistency. Add 15 ml. of the acidulated alcohol and filter through a weighed Gooch crucible. Wash free from platinum salts with 87.5 per cent alcohol solution, then with the ammonium chloride solution (saturated with potassium chloroplatinate), and finally with the 87.5 per cent alcohol solution. Dry the crucible and contents for an hour at 100°–110° C., cool in a desiccator and weigh as potassium chloroplatinate ($K_2PtCl_6$). Calculate the potassium as percentage of potassium oxide ($K_2O$).

The sodium is then obtained by difference. Calculate the amount of potassium as potassium chloride. Subtract the potassium chloride found from the combined weight of sodium and potassium chlorides to obtain the weight of sodium chloride. Calculate the sodium present as percentage of sodium oxide ($Na_2O$).

## HYDROGEN-ION CONCENTRATION OF SOIL

*Procedure.* Place 10 grams of soil (ground to pass a 40-mesh sieve) into a glass vial and add 10 ml. of water. Allow to stand 30 min. with intermittent agitation. Determine the $p$H of this suspension potentiometrically using a glass electrode (see p. 143).

## CHAPTER XVI

## FERTILIZERS AND LIMESTONE

Fertilizers, according to Wiley, are those materials which are added to soils to supply supposed deficiencies in plant foods, or to render more available the stores already present. The elements most frequently lacking in agricultural soils and consequently of greatest importance as fertilizer constituents are nitrogen, phosphorus, and potassium. These elements exist in the mineral form usually as nitrate or ammonium, phosphate, and potassium salts. When these elements are present in organic compounds, they are converted by soil organisms into the mineral form, before they are available to the plants. Due to its correcting influence on soil acidity, lime makes other soil constituents more available to the plant as well as also serving as a fertilizer.

Fertilizers may be obtained from natural sources and waste by-products, or they may be manufactured. The fertilizers from natural sources have accumulated in large deposits over certain geological periods in the earth's history. Examples of these are the deposits of Stassfurt salts, rock phosphates, and Chile saltpeter. Of the by-product fertilizers may be mentioned manure from the farm, dried blood and tankage from slaughter houses, and basic slag from the steel industry. Ammonia obtained from the distillation of bituminous coal or synthesized from the elements is manufactured into ammonium salts. Still other nitrogen-fixation processes manufacture nitrates from the nitrogen and oxygen of the air, and calcium cyanamide from calcium carbide and nitrogen from the air.

Fertilizers are evaluated on the basis of their percentage composition of fertilizing elements, their availability to the plant (largely dependent upon their solubility in the soil solution), and the absence of injurious constituents. The approximate percentages of each of the three principal fertilizing elements present in a number of commercial fertilizers are given in Table 24. The common fertilizers containing ammonium, nitrate, and potassium salts are soluble and readily available to the plant. The organic fertilizers and calcium cyanamide are slower acting because they must be made available through the action of the soil organisms. The

TABLE 24. APPROXIMATE PERCENTAGES OF THE THREE ESSENTIAL ELEMENTS IN SEVERAL COMMERCIAL FERTILIZERS

| Fertilizers | N (per cent) | $P_2O_5$ (per cent) | $K_2O$ (per cent) |
|---|---|---|---|
| Ammonium nitrate | 35 | | |
| Ammonium sulfate | 20–21 | | |
| Calcium cyanamide | 21–24 | | |
| Calcium nitrate | 15–17 | | |
| Sodium nitrate | 15–16 | | |
| Urea | 46 | | |
| Fresh farm manure | 0.6 | 0.1–0.3 | 0.4–0.7 |
| Dried blood | 10–16 | | |
| Tankage | 4–12 | 3–12 | |
| Cottonseed meal | 6–7 | 2–3 | 1.5–2.0 |
| Bone meal | 2–4 | 20–28 | |
| Rock phosphate | | 25–38 | |
| Superphosphate 16% | | 16 | |
| Superphosphate 18% | | 18 | |
| Superphosphate 20% | | 20 | |
| Treble superphosphate | | 43–46 | |
| Potassium chloride | | | 50–62 |
| Potassium sulfate | | | 50–53 |

phosphate fertilizers vary considerably in their availability due to great differences in their solubility. Rock phosphate, $Ca_3(PO_4)_2$, is relatively insoluble and consequently is a very slow acting fertilizer. Treatment of the rock phosphate with sulfuric acid gives acid phosphates which are more soluble and hence more available to the plant.

The analyst should know the origin of the fertilizer, since the methods for the determination of an element differ with the state of chemical combination in which the element is present. For example, quite different analytical procedures are required for the determination of nitrogen in the reduced form (ammonia or amino-nitrogen) than in the oxidized form (nitrate-nitrogen). Furthermore, it is also essential to be able to differentiate between the readily available fertilizing elements and those not readily available in order to interpret correctly the analytical values obtained.

## THE ANALYSIS OF FERTILIZERS

Only a few of the more common methods used in the analysis of fertilizers will be discussed. Complete methods for fertilizer analysis may be found in the "Official and Tentative Methods of Analysis" of the Association of Official Agricultural Chemists, 5th Ed., pages 20–40 (1940).

**Preparation of the Sample for Analysis.** Obtain a representative sample of the fertilizer, mix it thoroughly, and pass the entire sample through a 10-mesh sieve before subdividing for analysis (grind if necessary). Read the general directions for sampling and quartering on pages 15–20. Reduce the sample to about 50–100 grams in size by alternate mixing and quartering. Sift this sample through a sieve having circular openings 1/25 in. (1 mm.) in diameter, breaking up the lumps with a pestle. Grind the portion remaining on the sieve until the entire sample has passed through. Grind and sift as rapidly as possible so that no change occurs in the moisture content during this operation. Mix the sample thoroughly and store in a well-stoppered bottle.

**Determination of Moisture.** The amount of moisture is determined by drying a weighed quantity of the fertilizer to constant weight in a drying oven.

*Procedure.* A 2.000 gram sample of the thoroughly mixed fertilizer is weighed into a previously heated and weighed dish. The sample is dried for 5 hours at 100° C., cooled in a desiccator and weighed. In the case of sodium nitrate or ammonium sulfate the drying temperature employed is 130° C. rather than 100° C. The loss in weight of the sample is calculated as moisture.

*Remarks.* As in the case of feedstuffs, moisture determined by heating methods may be due to absorbed water, adsorbed or "bound" water, ammonia, and to the decomposition of organic matter (read pages 181–185 for discussion on moisture analyses). In the case of fertilizers containing volatile compounds and ammonia such as manure, drying at room temperature in a vacuum desiccator over concentrated sulfuric acid is preferable to drying at an elevated temperature.

**Determination of Total Phosphorus.**[1] The sample is dissolved and all organic matter destroyed.

In the gravimetric analysis, the phosphorus is precipitated as ammonium phosphomolybdate, filtered, washed free from impurities and redissolved. The phosphorus is then precipitated as magnesium ammonium phosphate, filtered, washed, and ignited to magnesium pyrophosphate. From the weight of magnesium pyrophosphate obtained, the amount of phosphorus present in the sample may be calculated.

In the volumetric analysis, the phosphorus is precipitated as ammonium phosphomolybdate, filtered, thoroughly washed free from impurities, and transferred back to the precipitating vessel. The milliliters of standard alkali required to just dissolve the ammonium phosphomolybdate precipitate is determined and, from this figure, the amount of phosphorus present may be calculated.

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[1] The method is essentially that present in the Assoc. Off. Agr. Chem., "Methods of Analysis," 5th Ed., 1940, pp. 21–23.

*Reagents.*

1. *Molybdate solution.* Dissolve 100 grams of molybdic acid in a mixture of 144 ml. of concentrated ammonium hydroxide and 271 ml. of water. Cool and pour this solution slowly, with constant stirring, into a mixture of 489 ml. of concentrated nitric acid and 1148 ml. of water. Keep the final mixture in a warm place for several days or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any sediment and preserve in a glass-stoppered vessel.
2. *Ammonium nitrate solution.* Dissolve 100 grams of ammonium nitrate, phosphate free, in water and dilute to 1 liter.
3. *Magnesia mixture.* Dissolve 55 grams of crystallized magnesium chloride in water, add 140 grams of ammonium chloride and 130.5 ml. of concentrated ammonium hydroxide, and dilute to 1 liter. Since a precipitate may form if this solution is stored for any length of time, the following alternate method of preparation is suggested. Dissolve 55 grams of crystallized magnesium chloride and 140 grams of ammonium chloride in water and dilute to 870 ml. Add concentrated ammonium hydroxide to each portion of the solution just before using, at the rate of 15 ml. per 100 ml. of solution.
4. *Ammonium hydroxide for washing.* Dilute 100 ml. of concentrated ammonium hydroxide with water to a volume of 1 liter. (This solution should contain not less than 2.5 per cent of ammonia by weight.)
5. *Magnesium nitrate solution.* Dissolve 150 grams of magnesium oxide in nitric acid (1:1), avoiding an excess of the acid; add a little magnesium oxide in excess; boil; filter from the excess of magnesium oxide, ferric oxide, etc.; and dilute to 1 liter.

*Preparation of the Sample for Analysis.* Dissolve as completely as possible (portions of certain samples will not dissolve in the reagents) a 2.5 gram sample of the fertilizer by one of the following methods:

1. Treat with 30 ml. of concentrated nitric acid and 5 ml. of concentrated hydrochloric acid and boil until all organic matter is oxidized (used when only a small amount of organic matter is present).
2. Dissolve in 20–30 ml. of concentrated hydrochloric acid and 5–10 ml. of concentrated nitric acid (used for samples containing considerable quantities of iron and aluminum phosphate).
3. Evaporate with 5 ml. of the magnesium nitrate solution; ignite the evaporated sample and dissolve the residue in concentrated hydrochloric acid (used for cottonseed meal and similar organic materials).
4. Digest the sample in a Kjeldahl flask with 20–30 ml. of concentrated sulfuric acid and 2–4 grams of sodium or potassium nitrate. The nitrate may be added in two portions, one at the beginning and the other near the end of the digestion; or in small quantities throughout the digestion period. When the solution becomes colorless (all organic matter oxidized) add 150 ml. of water and boil for a few minutes.

After the fertilizer sample has been dissolved by one of these methods, it should be cooled, diluted to 250 ml. with water and filtered. Discard the first 15 ml. of filtrate and preserve the rest in a stoppered bottle.

*For class work,* pure inorganic samples of soluble phosphates may be distributed for analysis. In this event, a sample not exceeding 0.5 gram in size is weighed into a beaker and dissolved in water and 10 ml. of concentrated nitric acid. The dissolved sample is then transferred to a 250 ml. volumetric flask and diluted to volume with water.

*Gravimetric Method.* Pipette an aliquot of the solution (prepared from the sample as previously directed) corresponding to 0.25, 0.50, or 1.0 gram into a 250 ml. beaker. Add concentrated ammonium hydroxide in slight excess and barely dissolve the precipitate formed with a few drops of concentrated nitric acid, stirring vigorously. If hydrochloric or sulfuric acid has been used as a solvent, add about 15 grams of crystalline ammonium nitrate or a solution containing that quantity. To the hot solution, add 70 ml. of the molybdate solution for every decigram of $P_2O_5$ present. Digest at 65° for 1 hour and determine whether or not the phosphorus has been completely precipitated by the addition of more molybdate solution to the clear supernatant liquid. Filter and wash with cold water or preferably with the ammonium nitrate solution. Dissolve the precipitate on the filter with ammonium hydroxide solution (1:1) and hot water, and wash into a beaker to a volume of not more than 100 ml. Neutralize with hydrochloric acid, using litmus paper or bromothymol blue as indicator. Cool, and from a burette add slowly (about 1 drop per second), stirring vigorously, 15 ml. of the magnesia mixture for every decigram of $P_2O_5$ present. After 15 min., add 12 ml. of concentrated ammonium hydroxide. Let stand until the supernatant liquid is clear (usually 2 hours), filter, and wash the precipitate with the dilute ammonium hydroxide wash solution until the washings are practically free from chlorides. Dry, burn first at a low heat and then ignite to constant weight preferably in a muffle furnace at 950°–1000° C. Cool in a desiccator and weigh as $Mg_2P_2O_7$. Calculate and report the result as percentage of $P_2O_5$.

*Volumetric Method.* This method is more rapid than the gravimetric and in the hands of an experienced analyst gives accurate results.

*Reagents.*

1. *Molybdate solution.* To 100 ml. of the molybdate solution (prepared as previously described under the gravimetric method) add 5 ml. of concentrated nitric acid. Filter this solution immediately before using.
2. *Standard sodium or potassium hydroxide solution.* Dilute 323.80 ml. of N alkali, free from carbonates, to 1 liter. One hundred milliliters of the solution should neutralize 32.38 ml. of N acid; 1 ml. = 1 mg. or 1 per cent of $P_2O_5$ on a basis of 0.1 gram of substance.
3. *A standard acid solution* of hydrochloric or nitric acid of equal or one half the strength of the standard sodium or potassium hydroxide solution.

*Procedure.* For percentages up to 5 use an aliquot corresponding to 0.4 gram of substance; for percentages between 5 and 20 use an aliquot corresponding to 0.2 gram of substance; and for percentages above 20 use an aliquot corresponding to 0.1 gram of substance. Add 5–10 ml. of concentrated nitric acid, depending on the method of solution (or the equivalent in ammonium nitrate); add concentrated ammonium hydroxide until the precipitate that forms dissolves slowly on vigorous stirring (or until the solution is just slightly acid to litmus paper); dilute to 75–100 ml.; and adjust to a temperature of 25°–30° C. For percentages below 5, add 20–25 ml. of the freshly filtered molybdate solution; for percentages between 5 and 20 add 30–35 ml. of the molybdate solution; and for percentages greater than 20, add sufficient molybdate solution to insure complete precipitation. Place the solution in a shaking or stirring apparatus and shake or stir for 30 min. at room temperature, decant *at once* through a filter; and wash the precipitate twice by decantation with 25–30 ml. portions of water, agitating thoroughly and allowing to settle. Transfer the precipitate to the filter and wash with cold water until the filtrate from two fillings of the filter yields a pink color upon the addition of phenolphthalein and 1 drop of the standard alkali solution. Transfer the precipitate and filter to the beaker or precipitating vessel, dissolve the precipitate in a small excess of the standard alkali, add a few drops of phenolphthalein indicator and titrate with the standard acid.

*Optional Volumetric Determination for Class Work.* Transfer a 50 ml. aliquot of the solution previously prepared for class work (p. 266) to a beaker. Neutralize with concentrated ammonium hydroxide using litmus paper and make slightly acid with 1–2 drops of concentrated nitric acid. Dilute to approximately 100 ml. and heat by immersing in a water bath at 60°–65° C. Add 50 ml. of the freshly filtered molybdate solution with constant stirring. Allow to stand in the water bath for 15 min., test for complete precipitation by the addition of a few drops of molybdate solution and filter at once. Wash twice by decantation using 25–30 ml. of water each time. Transfer as much of the precipitate as possible to the filter without the use of a policeman. Wash the beaker, filter, and precipitate with cold carbon dioxide-free water (recently boiled) until the filtrate from two fillings of the filter yields a pink color upon the addition of phenolphthalein and 3 drops of standard 0.1 N alkali solution.

Transfer the precipitate and filter to the beaker in which the precipitation occurred. Add 4 drops of phenolphthalein and titrate to a pink color with standard 0.1 N alkali solution, then add 5 ml. in excess. Let stand 10 min. and back-titrate the excess of alkali with standard 0.1 N acid solution.

From the titration figures and the weight of sample in the aliquot, calculate the percentage of $P_2O_5$ present in the sample.

*Remarks on the Phosphorus Determination.* Phosphate salts of the alkaline metal group are soluble and may be precipitated from solution as magnesium ammonium phosphate by the addition of magnesium chloride and ammonium hydroxide.

$$Na_3PO_4 + MgCl_2 + NH_4OH \rightarrow MgNH_4PO_4 + 2\,NaCl + NaOH.$$

Precipitated magnesium ammonium phosphate always contains varying amounts of water of crystallization so that it is difficult to determine its accurate weight by drying. Upon ignition, it is converted to the magnesium pyrophosphate which can be determined readily by weighing.

$$2\ MgNH_4PO_4 \xrightarrow{\Delta} Mg_2P_2O_7 + 2\ NH_3 + H_2O.$$

The concentrations of ammonium hydroxide and ammonium salts are regulated within definite limits. This is necessary to insure that phosphates other than the magnesium ammonium phosphate (which are not converted to the pyrophosphate on ignition) do not precipitate.

Insoluble tricalcium phosphate, $Ca_3(PO_4)_2$, requires different treatment from that accorded the soluble phosphates. If the tricalcium phosphate, dissolved in acid solution, were precipitated by a magnesium precipitation, the precipitate would be a mixture of the calcium and magnesium phosphates. To eliminate this difficulty, the phosphorus is removed from the calcium. This is accomplished by converting the tricalcium phosphate to ammonium phosphate by treatment with nitric acid and ammonium hydroxide. The ammonium phosphate, upon treatment with ammonium molybdate solution, gives a precipitate of ammonium phosphomolybdate.

$$\begin{aligned}(NH_4)_3PO_4 + 12(NH_4)_2MoO_4 + 24\ HNO_3 \rightarrow \\ (NH_4)_3PO_4 \cdot 12\ MoO_3 + 24\ NH_4NO_3 + 12\ H_2O.\end{aligned}$$

The precipitate is less soluble in solutions of ammonium nitrate and ammonium molybdate than in water and so these salts should be present in excess. The precipitation also takes place more readily in the presence of ammonium nitrate. Since an acid reaction is required and the precipitate is appreciably soluble in mineral acids, only a slight excess of nitric acid should be present. Nitric acid exerts less solvent action on the precipitate than either hydrochloric or sulfuric acids. A temperature of 65° is employed since the precipitate forms more readily at this temperature than at room temperature. A higher temperature must be avoided or molybdic anhydride may precipitate.

The ammonium phosphomolybdate precipitate is filtered and washed free from all interfering alkaline earth metals. Solution of the precipitate is effected by the addition of ammonium hydroxide forming the soluble ammonium phosphate and ammonium molybdate. This reaction also serves as the basis for the volumetric phosphorus determination.

$$(NH_4)_3PO_4 \cdot 12\ MoO_3 + 24\ NH_4OH \rightarrow (NH_4)_3PO_4 + 12\ (NH_4)_2MoO_4 + 12\ H_2O.$$

The ammonium phosphate, freed from the alkaline earth metals, may now be treated with the magnesium salt and converted to the magnesium ammonium phosphate. Ignition of this product yields the stable magnesium pyrophosphate. The addition of a large excess of magnesia mixture should be avoided since it may cause magnesium hydroxide and molybdic anhydride to precipitate with the magnesium ammonium phosphate.

**Nitrogen.** The nitrogen of fertilizers may be present in the reduced or oxidized form. In the protein matter of animal and vegetable substances, it is present in the reduced form as protein or amino nitrogen. Ammonium salts also contain nitrogen in the reduced form. In the salts of nitric acid, e.g., sodium, potassium and calcium nitrate, the nitrogen is present in the oxidized form.

Nitrogen present in the reduced form either as protein nitrogen or ammonium salts may be determined by the ordinary Kjeldahl method. If the nitrogen is present in the oxidized form as nitrate nitrogen, it must first be converted to the reduced form before it may be determined by the Kjeldahl procedure.

**The Determination of Total Nitrogen in the Absence of Nitrates (Organic and Ammoniacal Nitrogen Only).** The principle and procedure employed are identical with those described under the general protein analysis (see pp. 151–158). A sample of from 0.4–3.5 grams is used, depending upon the nitrogen content of the fertilizer.

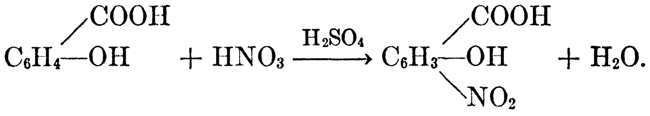
**The Determination of Total Nitrogen when Nitrates Are Present (The Kjeldahl Method Modified to Include the Nitrogen of Nitrates).** The nitrate is converted to nitric acid which, in the presence of concentrated sulfuric acid, nitrates the added salicylic acid forming nitro salicylic acid. The addition of a reducing agent, sodium thiosulfate or zinc, reduces the nitro group to an amine group forming amino salicylic acid. This compound is digested with boiling concentrated sulfuric acid in the presence of an oxidizing catalyst until all organic matter is oxidized. In this process, the amino-nitrogen is converted into ammonium sulfate. Upon heating the ammonium sulfate with alkali, ammonia is liberated and absorbed in standard acid. From the amount of standard acid neutralized by the liberated ammonia, the amount of nitrogen present in the fertilizer may be calculated.

*Digestion Procedure.* Weigh accurately a sample of 0.4–3.5 grams of the fertilizer, according to its nitrogen content, and wrap it tightly in a piece of filter paper. Drop the wrapped sample into a Kjeldahl digestion flask. Add 30 ml. of concentrated sulfuric acid containing 1 gram of salicylic acid and mix thoroughly with the sample. Allow to stand for 30 min. or longer, shaking at frequent intervals. Add 5 grams of sodium thiosulfate crystals, place on the digestion rack and heat for 5 minutes. Cool, add 15 grams of potassium sulfate or anhydrous sodium sulfate, 0.1–0.3 gram of copper sulfate and heat over a low flame until all danger from frothing has passed. Increase the heat and continue with the digestion, distillation, and titration as in the regular Kjeldahl process (pp. 153–158). A blank determination is also conducted to correct for the amount of nitrogen in the reagents.

*Remarks.* The nitrate present reacts with the sulfuric acid to give nitric acid:

$$2\,NaNO_3 + H_2SO_4 \rightarrow 2\,HNO_3 + Na_2SO_4.$$

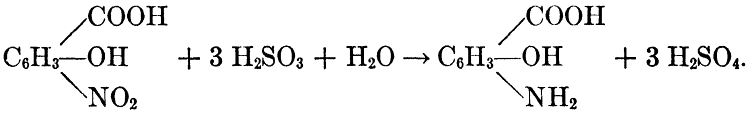
The nitric acid formed, in the presence of the concentrated sulfuric acid, nitrates the added salicylic acid:



$$C_6H_4\begin{cases} COOH \\ OH \end{cases} + HNO_3 \xrightarrow{H_2SO_4} C_6H_3\begin{cases} COOH \\ OH \\ NO_2 \end{cases} + H_2O.$$

The nitro compound is then reduced to an amino compound by the sodium thiosulfate in the presence of sulfuric acid:

$$Na_2S_2O_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2SO_3 + S$$



$$C_6H_3\begin{cases} COOH \\ OH \\ NO_2 \end{cases} + 3\,H_2SO_3 + H_2O \rightarrow C_6H_3\begin{cases} COOH \\ OH \\ NH_2 \end{cases} + 3\,H_2SO_4.$$

The amino compound is then oxidized by the sulfuric acid and the nitrogen converted to ammonium sulfate. From here on, the procedure is identical with the regular Kjeldahl procedure.

**Potassium.**[1] Potassium may be present in cottonseed meal and tobacco stem fertilizers in an organic combination. When organic matter containing potassium is ashed, the ash will contain the potassium as the oxide or carbonate. From mineral deposits, such as the Stassfurt salts, the potassium is obtained as the chloride or sulfate.

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[1] The method is essentially that present in the Assoc. Off. Agr. Chem., "Methods of Analysis," 5th Ed., 1940, pp. 30–31.

In the potassium determination it is essential that all organic matter be destroyed and that the potassium be converted to a soluble form. This is accomplished by a preliminary treatment of the fertilizer. The preliminary treatments will vary for different fertilizers depending upon the form in which the potassium is found.

**Determination of Potassium by Lindo-Gladding Method.** The sample is dissolved and all organic matter is destroyed. Elements such as calcium and aluminum are precipitated as the oxalate and removed. The potassium is converted to the sulfate and precipitated as potassium chloroplatinate. This is washed into a Gooch crucible with 80 per cent alcohol, dried and weighed. From the weight of potassium chloroplatinate obtained, the amount of potassium may be calculated by multiplying by the appropriate factor.

*Reagents.*

1. *Ammonium chloride solution.* Dissolve 100 grams of ammonium chloride in 500 ml. of water, add 5–10 grams of pulverized potassium chloroplatinate ($K_2PtCl_6$) and shake at intervals for 6–8 hours. Allow the mixture to settle over night and filter. The residue may be used for the preparation of a fresh supply.
2. *Platinum solution.* A platinum chloride ($PtCl_4$) solution containing the equivalent of 1 gram of metallic platinum (2.1 grams of $H_2PtCl_6$) in every 10 ml. For materials containing less than 15 per cent of potassium oxide ($K_2O$), a platinic chloride solution containing 0.2 gram of metallic platinum (0.42 gram of $H_2PtCl_6$) in each 10 ml. is recommended.
3. *An 80 per cent ethyl alcohol solution*—specific gravity$^{20^\circ}_{4^\circ}$ 0.8593.
4. *Sulfuric acid solution (1:1)* prepared by adding 1 volume of concentrated sulfuric acid to 1 volume of water.

*Preparing the Sample for Analysis.*

1. Mixed fertilizers. Weigh a 2.5 gram sample into a 12.5 cm. filter paper and wash with successive small portions of boiling water into a 250 ml. volumetric flask until about 200 ml. of filtrate are obtained. To the hot solution, add a slight excess of ammonium hydroxide and sufficient saturated ammonium oxalate solution to precipitate all the lime present. Cool, dilute to 250 ml., mix, and filter through a dry filter.

2. Potash salts; muriate and sulfate of potash; sulfate of potash and magnesia; and kainit. Dissolve a 2.5 gram sample and dilute to a volume of 250 ml. without treatment with ammonium hydroxide or ammonium oxalate.

3. Organic compounds. To obtain the total amount of potassium oxide in organic substances such as cottonseed meal, tobacco stems, etc., 10 grams of the sample are saturated with concentrated sulfuric acid and ignited in a muffle furnace at a low red heat to destroy the organic matter. Add a little concentrated hydrochloric acid, warm slightly in order to loosen the mass from the dish, transfer to a 500 ml. volumetric flask, add ammonium hydroxide and saturated ammonium oxalate solution, cool, dilute to 500 ml., mix, and filter through a dry filter.

4. Ashes from wood, cotton hulls, etc. Boil 10 grams of the sample with 300 ml. of water for 30 min. and add to the hot solution a slight excess of ammonium hydroxide and then sufficient saturated ammonium oxalate solution to precipitate all the lime present. Cool, dilute to a 500 ml. volume, mix, and filter through a dry filter.

*Procedure for Mixed Fertilizers, Organic Compounds, and Water Soluble Potash in Ashes from Wood, Cottonseed Meal, Etc.* A 50 ml. aliquot of the solution, prepared as previously directed, is evaporated nearly to dryness. Add 1 ml. of sulfuric acid solution (1:1), evaporate to dryness and ignite to whiteness. Maintain a full red heat until the residue is perfectly white. Dissolve the residue in hot water using at least 20 ml. for each decigram of potassium oxide present, and add a few drops of concentrated hydrochloric acid and then an excess of the platinum solution. Evaporate on a water bath to a thick paste, avoiding exposure to ammonia. Treat the residue with the 80 per cent alcohol. Filter on a previously prepared Gooch crucible and wash the precipitate thoroughly with 80 per cent alcohol, both by decantation and on the filter, continuing the washing after the filtrate is colorless. Then wash 5–6 times with 10 ml. portions of the ammonium chloride solution to remove impurities from the precipitate. Wash again thoroughly with the 80 per cent alcohol and dry the precipitate for 30 min. at 100° C. Weigh and calculate as $K_2O$. The precipitate should be completely soluble in water.

*Procedure for Muriate of Potash.* To a 50 ml. aliquot of the solution prepared as previously described, add a few drops of concentrated hydrochloric acid, 10 ml. of the platinum solution and evaporate to a thick paste. From this point proceed as directed for mixed fertilizers.

*Procedure for Sulfate of Potash, Sulfate of Potash and Magnesia, and Kainit.* To a 50 ml. aliquot of the solution prepared as previously described, add a few drops of concentrated hydrochloric acid and 15 ml. of the platinum solution. Evaporate to a thick paste and proceed as directed for mixed fertilizer except that 25 ml. portions of the ammonium chloride solution are used.

*Conversion factors:*

| | |
|---|---|
| $K_2PtCl_6$ to KCl | use 0.3065 |
| $K_2PtCl_6$ to $K_2SO_4$ | use 0.35843 |
| $K_2PtCl_6$ to $K_2O$ | use 0.19376 |

*Remarks.* In the preparation of the samples for analysis, treatment with ammonium hydroxide and ammonium oxalate precipitates all the bases present except magnesium. A large excess of ammonium oxalate should be avoided due to the difficulty attending its complete volatilization. There is also a tendency on the part of aluminum and iron hydroxide precipitates to occlude potassium salts. This may be prevented by adding the precipitating agent slowly with stirring.

The precipitation of the potassium should occur in a rather dilute solution. If potassium is precipitated from a solution which is too concentrated, it is very difficult to remove all the water from the precipitate upon drying. The reaction involved in the precipitation is:

$$2\,KCl + H_2PtCl_6 \rightarrow K_2PtCl_6 + 2\,HCl.$$

Ammonia in the presence of platinic chloride will form ammonium chlorplatinate which is relatively insoluble in alcohol. Because of this fact, the removal of all ammonium salts by heating precedes the precipitation of the potassium chlorplatinate. It is necessary, when evaporating the solution containing the potassium chlorplatinate precipitate, to protect the solution against ammonia fumes. For the same reason it is also necessary to wash the potassium chlorplatinate precipitate free from all platinic chloride with alcohol, before washing with the ammonium chloride solution.

Potassium chlorplatinate is somewhat soluble in a solution of ammonium chloride, consequently the ammonium chloride wash solution is saturated with potassium chlorplatinate. The potassium chlorplatinate precipitate is washed with the ammonium chloride solution to remove any magnesium salts which might be present.

Save the filtrate and washings from the precipitated potassium chlorplatinate and recover the platinum.

## LIMESTONE

The term limestone is applied to all calcium carbonate minerals which upon ignition give lime (CaO) of varying purity. Limestone consists primarily of impure calcium carbonate with varying amounts of magnesium carbonate, silica and silicates, and compounds of iron, aluminum, manganese, titanium, and other elements in small quantities. Limestones which contain a high percentage of magnesium carbonate are referred to as dolomitic limestones.

## ANALYSIS OF LIMESTONE

**Preparation of Sample.** Secure a representative sample (see pp. 15–20) and grind in a porcelain mortar or porcelain ball-mill to pass a 60-mesh sieve. Mix thoroughly and store in an air-tight container.

**Neutralizing Value.** Accurately weigh an exactly 1.000 gram sample of the ground limestone into a 400 ml. beaker. Add 150.0 ml. of 0.2000 N nitric acid, cover the beaker with a watch glass, and heat gently until solution is complete. Cool, add a few drops of methyl orange indicator solution, and titrate the excess acid with 0.2000 N sodium hydroxide solution. Calculate the neutralizing value in terms of percentage calcium carbonate ($CaCO_3$). If an exactly 1.000 gram sample was used and the nitric acid and sodium hydroxide solutions used were exactly 0.2000 N, then the percentage of calcium carbonate is numerically equal to the milliliters of nitric acid solution minus the milliliters of sodium hydroxide solution used for back titration.

**Moisture.** Dry 5 gram samples of the ground limestone to constant weight at 105° C. and report loss in weight as moisture.

**Loss on Ignition.** This is due mainly to the carbon dioxide expelled in converting carbonates to oxides and, to a lesser extent, the moisture present. Of minor importance is the oxidation of sulfides and ferrous salts, decomposition of sulfates, and volatilization of potassium chloride. In addition, ignition aids in making certain silicates more soluble in acids through the conversion of these silicates into calcium and magnesium salts by reaction with the oxides of the metals.

Weigh accurately, by difference, 0.7 gram samples into previously ignited and weighed platinum or porcelain crucibles. Cover the crucible and cautiously heat over a burner, starting with a low flame and increasing the size of the flame gradually until the bottom of the crucible is a dull red (approximately 5–10 min. heating period). The greater share of the carbon dioxide should be expelled in this heating which prevents mechanical loss in subsequent heating at high temperatures. Support the crucible upright in a silica triangle and direct the full heat of a burner against the bottom and one side of the crucible for 10 min. Cool in a desiccator and weigh. Reheat for 10-min. periods until constant weight is attained. Calculate and report the percentage loss on ignition.

**Silica.** Thoroughly transfer the ignited sample from the crucible into a 400 ml. beaker containing approximately 10 ml. of water. Add 1–2 ml. of hydrochloric acid (1:1) to the crucible, heat gently, pour into the beaker, and rinse the crucible thoroughly, collecting the washings in the beaker. Slowly transfer 20 ml. of hydrochloric acid to the beaker, cover with a watch glass, and digest on the steam bath. Upon complete disintegration of the sample, rinse off the watch glass and sides of the beaker. Put three bent glass hooks around the rim of the beaker, replace the watch glass now resting on the glass hooks, and evaporate to dryness on the steam bath. Cool, add 10 ml. of concentrated hydrochloric acid and place on the steam bath for a short time, then add 20 ml. of water and bring to a boil. Decant the solution into a small ashless filter paper, collecting the filtrate in a 400 ml. beaker. To the insoluble matter in the original beaker, add 20 ml. of hydrochloric acid (1:9) and boil for approximately 5 min. Filter through the same filter paper previously used. Transfer the entire residue to the filter and wash ten times with hydrochloric acid (1:100). Save the filter and contents.

Place the beaker containing the filtrate and washings on the steam bath and evaporate to dryness. Heat until no fumes of acid are noticeable from the beaker. Transfer to an oven at 140° C. and heat for 1 hour. Cool, add 10 ml. of hydrochloric acid, digest for a short time, add 20 ml. of water, and bring to a boil. Filter and wash as previously described, collecting the filtrate and washings. Transfer both filter papers to a platinum or porcelain crucible and ignite with a plentiful access of air to prevent the formation of a carbide of silicon. Complete the ignition by a 10-min. heating with the full heat of a burner. Cool, weigh, and reheat until constant weight is attained. Calculate and report as percentage of impure silica in the sample.

**Combined Oxides of Iron, Aluminum and Manganese ($R_2O_3$).** Dilute the filtrate and washings from the silica determination to 200 ml. Add just sufficient ammonium hydroxide to give the solution a faint odor of ammonia. Oxidize the iron and manganese by the addition of a few milliliters of bromine water and by boiling for several minutes. Add a little more ammonium hydroxide solution to keep the solution slightly ammoniacal and some ammonium chloride to prevent the precipitation of magnesium hydroxide. Filter the warm solution through an ashless filter paper and wash the precipitated hydroxides with several portions of hot water until free from chlorides. For accurate work, the precipitate should be redissolved and reprecipitated. Dry the filter and ignite to the oxides. Complete the ignition to constant weight by 5–10 min. heating periods with the full heat of a burner . Calculate and report as percentage of combined oxides ($R_2O_3$) in the sample.

**Calcium.** Add 2 drops of methyl orange indicator and acidify the filtrate from the $R_2O_3$ determination with dilute hydrochloric acid. If necessary, concentrate the filtrate to 200–250 ml. Heat to boiling and add 50 ml. of an ammonium oxalate solution (4 grams $(NH_4)_2C_2O_4 \cdot H_2O$ in 100 ml. of water) slowly with stirring. If any precipitation occurs, dissolve the precipitate by the addition of the smallest volume of hydrochloric acid solution. By means of a pipette, add dilute ammonium hydroxide solution, drop by drop, until the odor of ammonia is detected from the solution. Digest on the steam bath for 1 hour and decant the supernatant liquid through a filter paper, retaining as much of the precipitate in the beaker as possible. Place the beaker containing the precipitate under the filter and dissolve the small quantity of precipitate in the filter with hot dilute hydrochloric acid. Wash the filter thoroughly with hot water. Dilute to a volume of approximately 200 ml., add 2 ml. of the ammonium oxalate solution, then, drop by drop, an ammonium hydroxide solution until the odor of ammonia is detected. Digest on the steam bath for 1 hour and filter through an ashless filter paper. Wash the precipitate until free from chlorides with hot water containing a small amount of ammonium hydroxide and 0.25 per cent ammonium oxalate. Dry the filter and ignite carefully over a burner. Complete the incineration by heating 10–15 min. with the full heat of the burner. Cool and weigh. Reheat for 10-min. periods until constant weight is obtained. Calculate and report the percentage of calcium oxide in the sample.

*Remarks.* The ammonium oxalate reagent is added to an acid solution to decrease co-precipitation. A double precipitation in this determination assures a complete separation from magnesium. A slight amount of ammonium oxalate is added to the wash water since the solubility of calcium oxalate is less in an ammonium oxalate solution than in water.

**Magnesium.** Acidify the filtrate and washings from the calcium determination with dilute hydrochloric acid and evaporate to dryness on the steam bath. Add 5 ml. of concentrated nitric acid and again evaporate to dryness, repeating this procedure several times.

Moisten the dried residue with a few milliliters of dilute hydrochloric acid and add 150 ml. of water. If any residue remains, remove by filtration. Bring to a boil and add 5 ml. of diammonium hydrogen phosphate solution (prepared by dissolving 25 grams of the salt in 100 ml. of water and filtering). Then add, drop by drop, a dilute ammonium hydroxide solution until alkaline, and finally 10 ml. of concentrated ammonium hydroxide soution.

Permit the precipitate to stand 10 hours or longer before filtering or, if desired, let stand in ice water for 4 hours. Decant the supernatant liquid through a filter paper. Dissolve the small amount of precipitate on the paper and also that in the beaker by pouring dilute hydrochloric acid on the filter and catching the solution in the beaker containing the bulk of the precipitate. Wash the filter thoroughly with small portions of water, keeping the volume of the final solution to approximately 100 ml. Heat to boiling, add 0.5 ml. of the diammonium hydrogen phosphate solution; then, drop by drop, dilute ammonium hydroxide solution with constant stirring until alkaline; and finally, 10 ml. of concentrated ammonium hydroxide solution. Leave the solution in ice water for 4 hours, filter through an ashless filter paper and wash with a 1 N ammonium hydroxide solution until free from chlorides. Dry the precipitate and carefully char the filter paper in an uncovered upright weighed crucible. Place the crucible in a slanting position and oxidize the carbon with a very small flame. Complete the ignition by heating with the full heat of the burner for 20-min. periods until constant weight is attained. From the weight of $Mg_2P_2O_7$ obtained, calculate and report the percentage of MgO in the sample.

*Remarks.* A large excess of phosphate ions is favorable to the precipitation of magnesium ammonium phosphate. The precipitate is soluble in acids so an excess of ammonium hydroxide is added. The ammonium hydroxide is added after the excess diammonium hydrogen phosphate to avoid the possible precipitation of $Mg_3(PO_4)_2$ which does not change upon heating. Precipitation of magnesium hydroxide is prevented by an excess of ammonium salts. An excess of phosphate, ammonium, and hydroxide ions decreases the solubility of the magnesium ammonium phosphate. Care is required in the ignition of the precipitate to prevent reduction of the phosphate.

# CHAPTER XVII

# INSECTICIDES AND FUNGICIDES

The control of insect and fungi destruction of food materials is an important problem of the agricultural and food industries. A conservative estimate of the loss in foodstuffs in the United States, due to insect depredations, is not less than $250,000,000 annually. To this should be added another $100,000,000 spent yearly for insecticides to control the insect pests. It has been estimated that insects in this country annually nullify the labor of one million men. These facts should illustrate the magnitude of the problem.

Several different methods for controlling insects present themselves, and the selection of the proper method depends upon the type of insect concerned as well as the nature of the foodstuff. Insects with biting mouth parts may be killed by poisoning the material they eat or by the use of a poison gas. Insects with sucking mouth parts may be poisoned by contact insecticides or by fumigation.

Arsenic constitutes the toxic principle of most commercial insecticides designed for use against insects with biting mouth parts. Some of these insecticides contain arsenic in the trivalent (reduced) form, derived from arsenious oxide ($As_2O_3$) or arsenious acid ($H_3AsO_3$). Metallic salts of arsenious acid are known as arsenites. Most of the insecticides, however, contain arsenic in the pentavalent (oxidized) form and are derived from arsenic oxide ($As_2O_5$) or arsenic acid ($H_3AsO_4$). The salts of this acid are known as arsenates. Paris green and calcium arsenite are examples of arsenite insecticides; whereas lead, calcium, magnesium and zinc arsenates are examples of arsenate insecticides.

Analytical procedures for the important constituents of only a few typical insecticides will be considered. For detailed methods of analysis of insecticides see the Association of Official Agricultural Chemists, "Methods of Analysis," 5th Ed., pages 44–79 (1940) and Frear's "Chemistry of Insecticides and Fungicides," D. Van Nostrand Co., Inc., (1942).

## PARIS GREEN

Paris green is prepared by heating together solutions of soda ash (commerical anhydrous sodium carbonate) and arsenious oxide, forming sodium arsenite. To this is added a solution of copper sulfate with thorough mixing. Acetic acid is added forming Paris green (aceto-arsenite of copper), which is then washed several times with water and finally dried and pulverized.

The composition of commercial Paris green ranges from 54 to 57 per cent total arsenious oxide, from 1.5 to 4.5 per cent water soluble arsenious oxide, and from 29 to 30 per cent copper oxide. Impurities in Paris green may include small amounts of sand, sodium sulfate and arsenious oxide.

Paris green is gradually being replaced by lead arsenate as a general all around insecticide. One disadvantage of Paris green is that it is more apt to cause arsenic burn on plants than the arsenate sprays. This is due to the fact that arsenite compounds, as a rule, contain more soluble arsenic, which is toxic to the plant. Also, Paris green is very heavy and, when suspended in water, tends to settle rapidly thereby causing uneven coverage when spraying unless the suspension is constantly agitated.

**Determination of Total Arsenic by the Distillation Method.** The method is based upon the fact that arsenious chloride is volatile and can be quantitatively distilled from solution. The insecticide sample is treated with cuprous chloride and hydrochloric acid, which reduces all penta-valent arsenic (oxidized form) to the trivalent (reduced form), and converts all the arsenic present to arsenious chloride ($AsCl_3$). This compound, being volatile, is distilled along with hydrochloric acid into cold water, in which it is absorbed. After neutralization of the acid, the solution is buffered with sodium bicarbonate and the arsenic titrated with standard iodine solution.

*Reagents.*

1. *Starch indicator solution* (see p. 101).
2. *An approximately 0.05 N iodine solution.* Refer to page 102, using one half the quantities of iodine and potassium iodide required for the preparation of a 0.1 N iodine solution. Standardize the iodine solution using arsenious oxide as a primary standard (see p. 102).
3. *Methyl orange indicator* prepared by dissolving 1 gram of methyl orange in water, diluting to a liter and filtering.
4. *Concentrated sodium hydroxide solution* prepared by dissolving 400 grams of sodium hydroxide in water and diluting to 1 liter.

Fig. 47 illustrates the apparatus used in the determination. The 500 ml. distilling flask is supported by a wire gauze fitting over a circular hole in an asbestos board of such a size that it keeps the flame from hitting the sides of the flask. The first of the two 500 ml. Erlenmeyer flasks contains 40 ml. of water, the second flask 100 ml. of water. These flasks are kept cold in a pan of ice water.

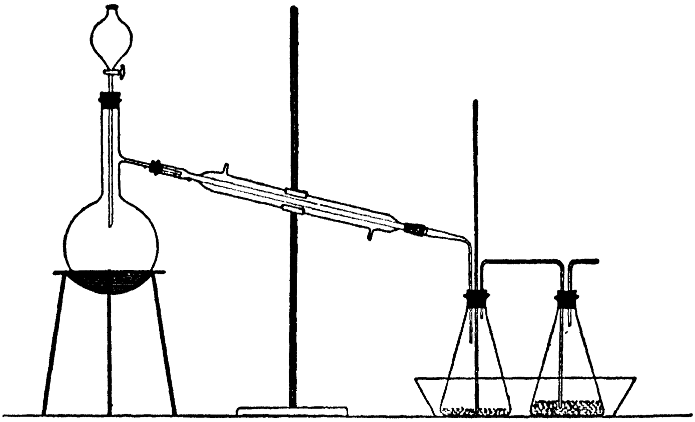

FIG. 47. Apparatus for Distillation of Arsenious Chloride. (From the Association of Official Agricultural Chemists' "Methods of Analysis.")

*Procedure.* Weigh accurately a 0.9000 gram sample of Paris green and wash it into the distilling flask with 100 ml. of concentrated hydrochloric acid. Add 5 grams of cuprous chloride and distill. As soon as the volume in the distilling flask is reduced to approximately 40 ml., add 50 ml. of concentrated hydrochloric acid by means of the dropping funnel. Continue the distillation and addition of 50 ml. portions of concentrated hydrochloric acid until 200 ml. of distillate have been obtained. Carefully wash down the condenser and all connecting tubes, allowing the washings to run into the Erlenmeyer flasks. Transfer the entire contents of the Erlenmeyer flasks to a liter volumetric flask, rinsing each flask several times to insure complete transfer of the solution. Dilute the solution to volume and mix thoroughly.

Pipette a 200 ml. aliquot of the solution into a 500 ml. Erlenmeyer flask. Add a few drops of phenolphthalein and nearly neutralize with the concentrated sodium hydroxide solution, being sure that the flask is kept cold. If the solution becomes alkaline, add sufficient hydrochloric acid to make it slightly acid. Carefully neutralize the solution with sodium bicarbonate (be sure to add the sodium bicarbonate slowly, with shaking) and then add 4–5 grams in excess. Titrate with the standard iodine solution, shaking continuously, until the end point is almost reached. Add 5 ml. of the starch indicator and continue the titration until a perceptible blue color persists for a minute.

From the volume of standard iodine solution used and the weight of sample represented in the aliquot, calculate the percentage of total arsenic in the sample.

*Remarks.* Cuprous chloride reduces any penta-valent arsenic to the tri-valent form which is more volatile. Arsenious chloride is volatile and is distilled into cold water in which it is absorbed. The water must be kept cold in order to reduce the volatility of the arsenious chloride. The volume of water added in the first receiving flask should not exceed 40 ml. in order to prevent the separation of an arsenic compound not readily redissolved without danger of some loss of arsenious chloride.

Sodium arsenite is oxidized by iodine to sodium arsenate:

$$Na_3AsO_3 + I_2 + H_2O \rightleftarrows Na_3AsO_4 + 2\ HI.$$

Only reactions which go to completion and not equilibrium reactions, such as this, may be used as the basis for quantitative procedures. To cause the above reaction to go to completion, the hydriodic acid must be destroyed as soon as it is formed. This is accomplished by adding an excess of sodium bicarbonate which acts as a buffer and neutralizes the acid as soon as it forms.

$$Na_3AsO_3 + I_2 + 2\ NaHCO_3 + H_2O \rightarrow Na_3AsO_4 + 2\ H_2CO_3 + 2\ NaI.$$

The cuprous chloride distillation method is a general method and may be used for the determination of total arsenic in Paris green, lead arsenate, calcium arsenate, zinc arsenite, magnesium arsenate and Bordeaux mixture with arsenicals. The method is not applicable in the presence of nitrates.

**The Determination of Total Arsenious Oxide ($As_2O_3$).** Dissolve a weighed quantity of the sample in an acid solution, neutralize with sodium bicarbonate insuring a definite excess, and add sufficient ammonium chloride to keep all the copper in solution. Titrate the arsenious oxide present in the solution as sodium arsenite with a standard iodine solution.

*Reagents.*

1. *Ammonium chloride solution* prepared by dissolving 250 grams of the salt in water and diluting to 1 liter.
2. *Dilute sulfuric acid solution (1:4)* prepared by adding 1 volume of concentrated acid to 4 volumes of water.

3. *Standard 0.1 N iodine solution.*
4. *Starch indicator solution* (see p. 101).

*Procedure.* Weigh accurately a 0.2–0.3 gram sample of Paris green into a 300 ml. Erlenmeyer flask. Add 10–15 ml. of dilute sulfuric acid (1:4) and 100 ml. of water. Heat on the steam bath until solution of the sample occurs. Cool and neutralize carefully with solid sodium bicarbonate (add the sodium bicarbonate slowly with constant shaking), finally adding 4–5 grams in excess. Add sufficient ammonium chloride solution to dissolve the precipitated copper. Dilute to an approximate volume of 200 ml. and titrate with standard 0.1 N iodine solution, shaking the flask continuously until the yellow color disappears but slowly from the solution when the iodine is added. Then add 5 ml. of starch indicator and continue adding the standard iodine solution slowly, with shaking, until a permanent purple-blue color is obtained. Correct for the milliliters of standard iodine solution necessary to produce a blue color with starch indicator in the presence of dissolved copper (using an equivalent weight of copper sulfate). From the corrected volume of standard iodine solution used and the weight of the sample, calculate the percentage of arsenious oxide ($As_2O_3$) present in the Paris green sample.

*Remarks.* Arsenic can be dissolved in sulfuric acid solution by heating on a steam bath without danger of volatilization of arsenic. Neutralization of the acid solution with sodium bicarbonate must be accomplished slowly. Carbon dioxide is liberated during the neutralization and, if this occurs too rapidly, the solution will foam over the top of the flask. The solution is neutralized when no carbon dioxide is evolved upon the further addition of sodium bicarbonate. The excess sodium bicarbonate acts as a buffer and neutralizes the acid formed in the titration of the arsenite with iodine.

Care must be exercised in the final titration of arsenite with the iodine solution. With care, a distinction can be made between the blue color of the copper in solution and the blue iodine-starch color. The blank determination should correct for the slight error involved due to individual ability to detect this difference.

**Determination of Total Cupric Oxide in Paris Green.** The copper is precipitated, dissolved in nitric acid forming copper nitrate, $Cu(NO_3)_2$, and then converted to copper acetate, $Cu(C_2H_3O_2)_2$. Upon treatment with potassium iodide, the copper liberates an equivalent amount of iodine which is titrated with standard sodium thiosulfate solution.

*Reagents.*

1. *An approximately 80 per cent acetic acid solution* prepared by adding 77 ml. of glacial acetic acid to 20 ml. of water.
2. *Dilute nitric acid solution (1:4)* prepared by adding 1 volume of concentrated acid to 4 volumes of water.
3. *A 2 per cent sodium hydroxide solution* prepared by dissolving 2 grams of sodium hydroxide in 98 grams of water.
4. *A 30 per cent potassium iodide solution* prepared by dissolving 30 grams of the salt in 70 grams of water.
5. *Standard 0.1 N sodium thiosulfate solution.*
6. *Starch indicator solution* (see p. 101).

*Procedure.* Weigh a 2.000 gram sample of the insecticide into a beaker, add 100 ml. of a 2 per cent sodium hydroxide solution and boil until all the copper is precipitated. Filter off the precipitate and wash it thoroughly with water. Place a clean beaker under the filter funnel and dissolve the precipitate in hot nitric acid (1:4). Cool the solution, transfer it to a 250 ml. volumetric flask and dilute to the mark. Remove a 100 ml. aliquot and evaporate to a volume of 3 ml. Add 50 ml. of water and neutralize with ammonium hydroxide solution, adding an excess. Boil the solution until it changes color and a partial precipitate forms, which is evidence that all excess ammonia has been driven off. Add 4 ml. of 80 per cent acetic acid, boil for 2 min. and cool. Add 10 ml. of a 30 per cent potassium iodide solution and titrate the liberated iodine with a standard 0.1 N sodium thiosulfate solution until the iodine color becomes faint yellow. Add 1 ml. of starch indicator and continue the titration slowly until the blue color disappears. From the milliliters of standard sodium thiosulfate solution used and the weight of sample present in the aliquot, calculate the percentage of copper oxide (CuO) in the sample.

*Remarks.* The copper present is precipitated as cuprous oxide and freed from impurities by filtration. The precipitate is readily dissolved in nitric acid. However, since a subsequent titration requires the presence of an organic acid and the absence of a mineral acid, the nitric acid must be eliminated. This is accomplished by evaporating the solution, adding ammonium hydroxide in excess, and boiling. The copper is then dissolved in acetic acid solution. The addition of potassium iodide effects a reduction of the copper with the liberation of an equivalent quantity of iodine.

$$2\,Cu(C_2H_3O_2)_2 + 4\,KI \rightarrow Cu_2I_2 + 4\,CH_3COOK + I_2.$$

An excess of potassium iodide is added so that sufficient potassium iodide will be contained in the final volume to hold all the liberated iodine in solution.

### LEAD ARSENATE

Arsenious oxide or white arsenic ($As_2O_3$) is used as the basis for the manufacture of all arsenicals. When white arsenic is treated with nitric acid, it is oxidized to arsenic acid ($H_3AsO_4$). This acid, upon treatment with a metallic oxide, is converted to the metallic arsenate.

The principal lead arsenate is acid lead arsenate ($PbHAsO_4$). At one time it was also known as neutral lead arsenate. This arsenate has the following theoretical composition: $As_2O_5$, 33.13%; PbO, 64.29%; and water of constitution, 2.58%. Acid lead arsenate is commonly made by mixing arsenic acid ($H_3AsO_4$) with litharge (PbO) in the presence of a small amount of nitric acid. However, other processes are also used for its preparation. Acid lead arsenate is a comparatively stable compound and but slightly soluble in water. Because of this, there is little danger of arsenic burn when it is applied to plants.

Although not as important commercially, basic lead arsenate is found on the market. It may be prepared by several different methods. Treatment of litharge (PbO) with acetic acid forms basic lead acetate, which mixed with arsenic acid, forms basic lead arsenate. It may also be prepared by mixing together sodium arsenate, litharge and nitric acid. Basic lead arsenate has the following theoretical composition: $As_2O_5$, 23.2%; PbO, 75%; and water of constitution, 1.8%.

**Determination of Total Arsenic.** Total arsenic is determined by the distillation method previously discussed on pages 280–282. A 1.500 gram sample of the lead arsenate is used for the determination.

**Determination of the Total Arsenic Oxide.** Dissolve the sample in hydrochloric acid, add potassium iodide, and titrate the liberated iodine with standard sodium thiosulfate solution using starch as indicator.

*Reagents.*

1. *Starch indicator* (see p. 101).
2. *Ammonium chloride solution.* Dissolve and dilute 250 grams of ammonium chloride to one liter with water.
3. *Potassium iodide solution.* Dissolve and dilute 20 grams of potassium iodide to 100 ml. with water.

4. *Standard iodine solution.* Prepare an approximately 0.05 N iodine solution according to the directions on page 102, using one half the quantities of iodine and potassium iodide required for a 0.1 N solution.
5. *Standard sodium thiosulfate solution.* Prepare an approximately 0.05 N thiosulfate solution according to the directions on page 104 using one half the quantity of sodium thiosulfate required for the 0.1 N solution.

*Procedure.* Weigh accurately about 0.5 gram of the well mixed and powdered sample into a 300 ml. Erlenmeyer flask. Add 30 ml. of concentrated hydrochloric acid and evaporate to dryness on the steam bath. Dissolve in 50 ml. of concentrated hydrochloric acid, heating on the steam bath if necessary. After cooling to room temperature, add 10 ml. of the potassium iodide solution, sufficient ammonium chloride solution to produce a clear solution (50 ml. or more), and immediately titrate the iodine liberated with the standard 0.05 N sodium thiosulfate solution. When the end point is almost reached (the solution is colored but faintly yellow), 150 ml. of water are added and the titration is continued slowly, using starch indicator.

*Remarks.* This method is based on the reaction: $As_2O_5 + 4\,HI \rightarrow As_2O_3 + 2\,H_2O + I_2$, which takes place quantitatively only in a strongly acid solution. Nitrates, if present, would cause an appreciable error. However, all nitric acid is expelled by evaporating to dryness on the steam bath with an excess of hydrochloric acid. This evaporation also decomposes lead peroxide which is sometimes present in lead arsenate. Care must be used when heating arsenic solutions with hydrochloric acid to avoid loss of arsenic by volatilization.

**The Determination of Total Lead Oxide.** Dissolve the sample in nitric acid and remove any insoluble matter by filtration. Nearly neutralize, and precipitate the lead with potassium chromate solution, forming the insoluble lead chromate. Filter through a Gooch crucible, wash, dry and weigh.

*Reagents.*

1. *Dilute nitric acid solution (1:4)* (see p. 284).
2. *Dilute nitric acid solution (1:9)* prepared by adding 1 volume of concentrated acid to 9 volumes of water.
3. *A 10 per cent potassium chromate ($K_2CrO_4$) solution* prepared by dissolving 10 grams of the salt in 90 grams of water.

*Procedure.* Accurately weigh approximately 0.5 gram of the well-mixed powdered sample into a 600 ml. beaker. Add 25 ml. of dilute nitric acid (1:4) and heat on a hot plate. Filter to remove any insoluble residue and dilute the solution to 400 ml. Heat to 80°–90° C., and add ammonium hydroxide solution until a slight precipitate forms. Add sufficient dilute nitric acid (1:9) to redissolve the precipitate and then add 1–2 ml. in excess. Still keeping the solution almost at the boiling point, add 50 ml. of a hot 10 per cent potassium chromate solution by means of a pipette, with constant stirring. While hot, decant the solution through a Gooch crucible (previously heated to 150° C. and weighed). Wash the precipitate several times by decantation and finally transfer to the Gooch filter with boiling water. Continue the washing with boiling water until the washings are colorless. Dry the crucible containing the lead chromate at 150° C. until a constant weight is obtained. From the weight of the lead chromate obtained, calculate the percentage of lead oxide in the sample using the factor 0.6906.

*Remarks.* A small amount of acid lead arsenate ($PbHAsO_4$) may precipitate along with the lead chromate causing slightly high results. This error, however, rarely amounts to more than 0.2%.

## BORDEAUX MIXTURE

A fungicide is any substance which is toxic to fungi. Bordeaux mixture, the first general fungicide used as a spray against fungous diseases of plants, is still more widely used than any other. It is especially useful in controlling late-blight of potatoes, black-rot of grapes and bitter-rot of apples.

Bordeaux mixture may be made by mixing copper sulfate and lime (either calcium oxide or hydroxide) in the presence of water. This gives a mixture of basic copper sulfates and calcium sulfate. The fungicidal properties are due to the copper ion.

Bordeaux mixture is considered a protectant fungicide. It is not sufficiently soluble in water to exert its fungicidal properties but requires the solvent action of compounds secreted by the plants or, possibly, even by the fungi themselves, before its fungicidal properties become evident.

**Determination of Copper.** The sample is dissolved and the copper present converted to cupric acetate. Upon treatment with potassium iodide, the copper is reduced and an equivalent amount of iodine is liberated, which is then titrated with standard sodium thiosulfate solution.

*Reagents.*

1. *An approximately 10 per cent nitric acid solution* prepared by adding 10 ml. of the concentrated acid to 86 ml. of water.
2. *A 30 per cent potassium iodide solution* prepared by dissolving 30 grams of the salt in 70 grams of water.
3. *Standard 0.1 N sodium thiosulfate solution.*
4. *Starch indicator solution* (see p. 101).

*Procedure.* Accurately weigh about 2 grams of the well-mixed sample into a beaker and dissolve in 50 ml. of 10 per cent nitric acid. Neutralize with ammonium hydroxide solution and add a few milliliters in excess. Boil until the excess ammonia is expelled and add sufficient acetic acid to clear the solution and then 5 ml. in excess. Cool the solution, add 10 ml. of 30 per cent potassium iodide solution and titrate with standard 0.1 N sodium thiosulfate solution using starch indicator. Calculate the percentage of copper present as copper oxide (CuO).

# PART VII

# STOICHIOMETRY

## CHAPTER XVIII

## SOLUTION OF PROBLEMS

To most students, the solution of analytical problems is the most difficult phase of quantitative analysis. Actually, however, the calculations involved in analytical work are not difficult and may be mastered readily by a reasonable amount of well directed study. Perhaps the greatest difficulty experienced by students is in completely understanding the problem to be solved. It is absolutely essential that every problem be understood thoroughly and its solution reasoned out before attempting the actual calculations. This fact cannot be stressed too highly. At the same time it should be emphasized that students *should not attempt to memorize* a set procedure or formula for working out a type of problem. If a problem is really understood, its solution may be reasoned out accurately without memorizing any set procedures.

Where chemical equations are involved in a problem, it is advisable to write such equations in balanced form before starting the actual calculations. While this may appear elementary at times, it helps in understanding the reactions involved and helps to keep the proper quantitative relationships of the various constituents with respect to each other.

While a thorough understanding of the problem and clear reasoning are required for its solution, the correct answer cannot be obtained without exercising the proper care and precision in the actual calculations. Carelessness in the placing of decimal points and errors in addition, subtraction, multiplication and division should not be dismissed lightly. *The correct solution of a problem demands the correct answer.*

The student who has mastered the art of working problems understands the problem, clearly reasons out the method for the solution of the problem, carefully works out the calculations involved, and obtains an answer which he knows is correct. In order to illustrate this sequence of procedures in the solution of a problem, a number of typical problems and their solutions will be presented.

**A. Since chemical compounds have a constant composition, it is possible to determine the percentage composition of the various elements within a compound, e.g.:**

1. *Calculate the percentage of Mg, S, and MgO in* $MgSO_4$. In a molecular weight of $MgSO_4$ (120.4 grams) there is one atomic weight of Mg (24.36 grams), one atomic weight of S (32.06 grams), and one molecular weight of MgO (40.36 grams).

The percentage of Mg in $MgSO_4$ =

$$\frac{24.36}{120.4} \times 100 = 20.23 \text{ per cent.}$$

The percentage of S in $MgSO_4$ =

$$\frac{32.06}{120.4} \times 100 = 26.63 \text{ per cent.}$$

The percentage of MgO in $MgSO_4$ =

$$\frac{40.36}{120.4} \times 100 = 33.52 \text{ per cent.}$$

Thus, since $MgSO_4$ always contains 20.23 per cent of magnesium, we may ascertain the amount of magnesium present in any known quantity of $MgSO_4$ by multiplying the weight of $MgSO_4$ by the decimal form of 20.23 per cent, namely 0.2023. This decimal expression of percentage composition may also be called a *chemical factor*. Chemical factors are especially valuable in gravimetric analysis, since only rarely are the substances to be determined weighed in the form in which the result is to be expressed. In general, the compounds actually weighed contain several other elements besides the one to be determined, and a chemical factor is employed to determine the actual amount of the element present, e.g.:

2. *In the determination of sulfur in a soluble sulfate, the sulfur is precipitated and weighed as barium sulfate. If a sample of soluble sulfate gave a precipitate of 0.4200 gram of barium sulfate, how many grams of sulfur were present in the sample analyzed?*

By inspection, it is noted that there is one atomic weight of sulfur present in a molecular weight of barium sulfate. The chemical factor for sulfur in barium sulfate is $\frac{32.06}{233.4}$ or 0.1373. Then to find the weight of sulfur equivalent to 0.4200 gram of barium sulfate:

$$0.4200 \text{ gram} \times 0.1373 = 0.0577 \text{ gram.}$$

Thus, the sample analyzed must have contained 0.0577 gram of sulfur in order to furnish sufficient sulfur to give a precipitate of 0.4200 gram of barium sulfate.

It should be emphasized that the relationship of the various elements to the total molecular composition must be carefully observed, e.g.:

3. *Calculate the grams of phosphorus present in 0.3000 gram of magnesium pyrophosphate* ($Mg_2P_2O_7$). By inspection, it will be noted that there are two atoms of phosphorus present in every molecule of the magnesium pyrophosphate. The chemical factor for phosphorus in magnesium pyrophosphate is then

$$\frac{2\ \mathrm{P}}{\mathrm{Mg_2P_2O_7}} = \frac{62.08}{222.7} = 0.2788.$$

Then, 0.3000 gram × 0.2788 = 0.0836 gram of phosphorus present in 0.3000 gram of magnesium pyrophosphate.

**B. Reactions which involve precipitations frequently require the calculation of the volume of precipitating agent necessary for a given reaction.** In problems of this type, it is essential to know whether the concentration of the solution is expressed in grams per definite volume, in percentage by weight, or in percentage by volume.

The following problem illustrates a case in which the concentration of the precipitating agent is expressed in grams per definite volume:

1. *Determine the milliliters of barium chloride solution, containing 10 grams of* $BaCl_2 \cdot 2\ H_2O$ *per 100 milliliters of solution, required to completely precipitate the sulfur in 0.2500 gram of potassium sulfate.*

$$\mathrm{K_2SO_4 + BaCl_2 \cdot 2\ H_2O = BaSO_4 + 2\ KCl + 2\ H_2O}.$$

From the above equation, it is evident that one gram molecule of $BaCl_2 \cdot 2\ H_2O$ is equivalent to 1 gram molecule of $K_2SO_4$. The weight of $BaCl_2 \cdot 2\ H_2O$ required to precipitate the sulfur in 0.2500 gram of $K_2SO_4$ may then be obtained from the following proportion:

$$\frac{\text{Mol. wt. } \mathrm{K_2SO_4}}{\text{Mol. wt. } \mathrm{BaCl_2 \cdot 2\ H_2O}} = \frac{\text{grams } \mathrm{K_2SO_4}}{\text{grams } \mathrm{BaCl_2 \cdot 2\ H_2O}} \text{ or } \frac{174.4}{244.3} = \frac{0.2500}{x},$$

where $x = 0.3500$ gram of $BaCl_2 \cdot 2\ H_2O$ required. Since the precipitating solution contains 10 grams of $BaCl_2 \cdot 2\ H_2O$ per 100 ml. of solution, 1 ml. of the solution will contain 10/100 gm. or 0.10 gram $BaCl_2 \cdot 2\ H_2O$. Dividing the total weight of $BaCl_2 \cdot 2\ H_2O$ required for precipitation by the weight of $BaCl_2 \cdot 2\ H_2O$ present in

1 ml. of the solution will give the number of milliliters of solution required for complete precipitation.

0.3500 ÷ 0.10 = 3.50 ml., the volume which will contain the 0.3500 gram of $BaCl_2 \cdot 2\,H_2O$ necessary to effect complete precipitation.

The following problem is similar to the preceding one except that the strength of the precipitating agent is expressed in terms of per cent by weight and specific gravity.

2. *Determine the milliliters of 10 per cent by weight barium chloride solution, Sp. Gr.*$^{15^\circ}_{4^\circ}$ *1.094, required to completely precipitate the sulfur in 0.2500 gram of potassium sulfate.*

As in the preceding problem it is evident that one gram molecule of $BaCl_2$ is equivalent to one gram molecule of $K_2SO_4$. The weight of $BaCl_2$ required to precipitate the sulfur in 0.2500 gram of $K_2SO_4$ may then be obtained from the following proportion:

$$\frac{\text{Mol. wt. } K_2SO_4}{\text{Mol. wt. } BaCl_2} = \frac{\text{grams } K_2SO_4}{\text{grams } BaCl_2}, \text{ or, } \frac{174.4}{208.3} = \frac{0.2500}{x},$$

where $x = 0.2986$ gram of $BaCl_2$ required.

Since true specific gravity is synonymous with density, the weight of 1 ml. of the $BaCl_2$ solution is 1.094 grams. However, only 10 per cent of this weight is $BaCl_2$, therefore:

1.094 grams × 0.10 =
0.1094 gram, the weight of $BaCl_2$ per ml. of the solution.

The weight of $BaCl_2$ required for precipitation, 0.2986 gram, divided by the weight of $BaCl_2$ per ml. of precipitating solution (0.1094 gram) will give the ml. of $BaCl_2$ solution required for the complete precipitation of the sulfur in 0.2500 gram of $K_2SO_4$.

0.2986 ÷ 0.1094 = 2.729 ml. of $BaCl_2$ solution required.

**C. The greater share of the problems involved in gravimetric analysis are percentage problems.** In general, the solution of percentage problems involves three steps:

1. Obtaining the weight of the sample.
2. Obtaining the weight of the constituent analyzed for.
3. The calculation of the percentage by the simple expression:

$$\frac{\text{Weight of constituent}}{\text{Weight of sample}} \times 100 = \text{per cent of constituent in the sample.}$$

If these steps are kept in mind, the solution of percentage problems becomes relatively easy.

*Calculate the percentage of chloride in a 0.2000 gram sample of mineral yielding a 0.5000 gram precipitate of silver chloride (AgCl).*

1. The weight of the sample is given as 0.2000 grams.

2. The weight of chloride present must be obtained from the data. By inspection, it is noted that there is one atom of chlorine for every molecule of silver chloride; therefore, the chemical factor for chlorine in silver chloride is

$$\frac{\text{Cl}}{\text{AgCl}} = \frac{35.46}{143.3} = 0.2475.$$

0.5000 gram × 0.2475 = 0.1238 gram of chloride present in the mineral sample.

3. $\frac{0.1238}{0.2000} \times 100 = 61.90$, the percentage of chloride in the mineral sample.

**D. Solutions may be expressed in percentage strength, either in percentage by weight or percentage by volume.** The former method of expression is the more common and it is usually understood that, unless otherwise specified, the percentage strength of a solution means per cent by weight, see page 59.

Problems involving per cent by weight and per cent by volume:

1. *A 10 per cent by volume alcohol-water solution* has a Sp. Gr.$^{15.5°}_{4°}$ *of 0.9866. Water at the same temperature has a density of 0.9991 and 100 per cent pure alcohol has a density of 0.7936. What is the per cent by weight of alcohol in the solution?*

If the unit of volume is taken as 1 ml., then by definition, the alcohol-water solution consists of 10 ml. of pure alcohol made up to a total volume of 100 ml.

0.7936 × 10 =
7.936 grams of pure alcohol present in 100 ml. of the solution.

0.9866 × 100 = 98.66 grams (the weight of the total solution).

7.936 ÷ 98.66 × 100 =
8.04 per cent (the per cent by weight of alcohol in the solution).

2. *A 35.00 ml. volume of pure alcohol with a specific gravity of 0.7851 at 25° C. was diluted to 250.0 ml. of solution with water having a specific gravity of 0.9971 at 25° C. Calculate the per cent by volume of the resulting alcohol-water solution and also the grams of alcohol per ml. of the solution.*

*a.* Since 35.00 ml. of the pure alcohol were diluted to a volume of 250.0 ml., then the percent by volume of alcohol would be:

$$\frac{35.00}{250.0} \times 100 = 14.00 \text{ per cent.}$$

*b.* A 35.00 ml. volume of alcohol with a specific gravity of 0.7851 at 25° C. would have a weight equivalent to 0.7851 gram × 35.00 or 27.48 grams. The weight of alcohol per milliliter of solution then would be:

$$\frac{27.48}{250.0} = 0.1099 \text{ gram.}$$

**E. Problems in volumetric analysis are frequently concerned with the determination of the normal factors of solutions.** These will be summarized briefly:

1. *If 10.00 ml. of a 0.1200 N solution exactly reacts with 11.00 ml. of a solution of unknown normality, calculate the normal factor of this latter solution.* Then since the volume of the one solution multiplied by its normal factor is equivalent to the volume of the other solution multiplied by its normal factor, we may write:

$$10.00 \times 0.1200 = 11.00 \times x \text{ or } \frac{10.00 \times 0.1200}{11.00} = x = 0.1091,$$

the normal factor of the unknown solution.

2. *Calculate the normal factor of an acid solution, if 30.00 ml. of the acid solution exactly neutralizes 0.2385 gram of sodium carbonate.*

A normal solution of sodium carbonate contains $\frac{Na_2CO_3}{2}$ or $\frac{106.0}{2} = 53.0$ grams of $Na_2CO_3$ per liter. One milliliter of a normal solution contains 1/1000 of this amount or 0.053 gram (the milliequivalent weight of $Na_2CO_3$). $0.2385 \div 0.053 = 4.50$ ml. of N $Na_2CO_3$ solution which will contain the 0.2385 gm. of $Na_2CO_3$.

Stating the problem in the form used above in 1, we get:

$$4.500 \times 1.000 = 30.00 \times x, \text{ or } x = \frac{4.500 \times 1.000}{30.00} =$$

0.1500, the normal factor of the acid solution.

3. *Calculate the normal factor of a sulfuric acid solution if 25.00 ml. of the acid solution give a precipitate of 0.3200 gram of barium sulfate.*

Stated in another way, 25.00 ml. of $x$ N sulfuric acid solution are equivalent to 0.3200 gram of barium sulfate. The equivalent weight of barium sulfate is one half its molecular weight or 116.7 grams, and its milliequivalent weight is 0.1167 gram. Then, 0.3200 ÷ 0.1167 = 2.742 ml. of 1 N barium sulfate solution represented in the weight of the precipitate. We may now write:

$$25.00 \times x = 2.742 \times 1$$

$$x = \frac{2.742 \times 1}{25.00} = 0.1097,$$

the normal factor of the sulfuric acid solution.

**F. At times, it is preferable to determine the *titer* of a solution instead of a normal factor.** *Using as an example the previous problem 2 under E (30.00 ml. of an acid solution neutralizes 0.2385 gram of $Na_2CO_3$), the sodium carbonate titer of the acid solution would be:* $\frac{0.2385}{30.00}$, or 0.00795; i.e., 1 ml. of the acid solution is equivalent to 0.00795 gram of sodium carbonate. With the titer expressed in grams of sodium carbonate when using the acid solution to titrate samples containing sodium carbonate, the grams of sodium carbonate represented by the titration value can be determined by a simple multiplication.

*Suppose it is desired to calculate the sodium chloride-titer of a 0.1053 N silver nitrate solution.* One milliliter of a 0.1053 N silver nitrate solution is equivalent to 1 ml. of a 0.1053 N sodium chloride solution. One ml. of 0.1053 N sodium chloride solution will contain 0.1053 × 0.05846 (the milliequivalent weight of sodium chloride), or 0.006156 gram of sodium chloride. Therefore the sodium chloride-titer of the standard silver nitrate solution is 0.006156.

**G. The strength of oxidizing and reducing solutions may be expressed in terms of a normal factor, or, in terms of the amount of oxygen available for oxidizing purposes, or amount of hydrogen available for reducing purposes.** Thus, for example, since 1 oxygen atom will oxidize 2 hydrogen atoms to form $H_2O$; the normal, or equivalent weight of oxygen is:

$$\frac{O}{2}, \text{ or } \frac{16}{2}, \text{ or } 8.000.$$

One ml. of a normal oxygen solution would then contain 8.00/1000 or 0.008 gram of oxygen (the milliequivalent weight of oxygen).

1. *If 10.00 ml. of a potassium permanganate solution were to contain 0.0400 gram of available oxygen in acid solution, calculate the normal factor of the potassium permanganate solution.* Then, 0.0400 ÷ 10.00 = 0.0040, the grams of oxygen contained in 1 ml. of the potassium permanganate solution. Dividing this weight by

the weight of oxygen in 1 ml. of a normal solution (the milliequivalent weight) will give the normal factor of the solution: $0.0040 \div 0.0080 = 0.5000$, the normal factor of the potassium permanganate solution.

**H. In the determination of the normal factor of a solution, using a primary standard, it is often desirable to know how much of the standard to use in the titration so that a reasonable volume (20–30 ml.) of the standard solution will be employed.** For example:

1. *An approximately 0.1 N acid solution is to be standardized against sodium carbonate as a primary standard. How large a sample of sodium carbonate should be weighed out so that approximately 25 ml. of the acid solution will be used in the titration?*

Assuming the acid solution to be exactly 0.1 N, then 25 ml. of the acid solution will be equivalent to 2.50 ml. of N acid solution and will exactly neutralize 2.50 ml. of N base, e.g., sodium carbonate.

The equivalent weight (normal weight) of sodium carbonate is:

$$\frac{Na_2CO_3}{2} = \frac{106.0}{2} = 53.00 \text{ grams.}$$

One milliliter of a 1.0 N solution will then contain 0.0530 gram of sodium carbonate. $0.0530 \times 2.50 = 0.1325$ gram, the weight of sodium carbonate contained in 2.50 ml. of 1 N or 25 ml. of 0.1 N $Na_2CO_3$ solution and which will exactly neutralize 25 ml. of 0.1 N acid solution.

**I. In the analysis of agricultural and biological products it is frequently necessary to convert values from one moisture to another moisture basis.** For example, a feed may be guaranteed to contain a definite percentage of protein on the basis that the feed contains 15 per cent moisture. However, when the feed is later analyzed it may only contain 8 per cent of moisture and the protein results obtained must be calculated to a 15 per cent moisture basis, if a comparison with the guaranteed values is to be made. For example:

*An air-dry feed upon drying in a moisture oven was found to contain 10.00 per cent of moisture. A 2.000 gram sample of the air-dry feed, upon ashing, was found to contain 0.0440 gram of ash. Calculate the percentage of ash on the original or air-dry basis and on a 15.00 per cent moisture basis.*

1. The percentage ash on the original basis may readily be calculated from the expression:

$$\frac{0.0440}{2.000} \times 100 = 2.20 \text{ per cent.}$$

2. Two general methods for calculating from one moisture to a different moisture basis are available:

*a.* $2.000 \times 0.10 = 0.2000$ gram, the moisture present in a 2.000 gram sample.

$2.000 - 0.200 = 1.800$ grams, the dry matter present in a 2.000 gram sample.

On a 15 per cent moisture basis, the 1.800 grams of dry matter would represent 100 − 15 or 85 per cent of the total weight of the sample, thus:

$1.800 \div 0.85 = 2.118$ grams, weight of sample with 15 per cent moisture, containing the same amount of dry matter (and consequently the same amount of ash) as the 2.000 gram sample with 10 per cent of moisture.

$0.0440 \div 2.118 \times 100 = 2.08$ per cent, the percentage of ash on a 15 per cent moisture basis.

*b.* In the problem, the percentage of ash on the original air-dry basis (10% moisture) was 2.20 per cent. A feed containing 10 per cent moisture would have 100 − 10 or 90 per cent dry matter; while a feed containing 15 per cent moisture would have 100 − 15 or 85 per cent dry matter. Then since the percentage of ash will vary directly with the percentage of dry matter present, the following proportion may be established:

$\frac{2.20}{90.0} = \frac{x}{85.0}$ or, $x = 2.08$ per cent, the percentage of ash on a 15 per cent moisture basis.

**J. In routine analytical work, frequently all the analyses made are of a particular type.** Under these conditions, valuable time may be saved and calculations simplified by using a certain definite weight of sample, or concentration of solution, so that the weight or titration value obtained in the analysis will represent numerically the percentage of the constituent analyzed for, without further calculation.

1. *Calculate the weight of sample of impure* $K_2CO_3$ *which must be weighed out so that when the solution is titrated with 0.2 N acid, the number of milliliters of acid used will be numerically equal to the percentage of* $K_2CO_3$.

Stating the problem in formula form will give:

$$\frac{1 \text{ ml.} \times 0.2(\text{N.F.}) \times 0.0691 \times 100}{x \text{ grams (sample weight)}} = 1.00 \text{ per cent,}$$

where 0.0691 is the milliequivalent weight of $K_2CO_3$, or the weight of $K_2CO_3$ in 1 ml. of a normal solution.

Solving for $x$: $1 \times 0.2 \times 0.0691 \times 100 = x$;

$$x = 1.382, \text{ the sample weight to be used.}$$

2. *Calculate the concentration of an acid in terms of normality so that if 1.000 gram of impure $K_2CO_3$ is used as a sample, the per cent of $K_2CO_3$ present will be numerically equal to the number of milliliters of acid used.*

Stating the problem in formula form will give:

$$\frac{1 \text{ ml.} \times x(\text{N.F.}) \times 0.0691 \times 100}{1.00} = 1.00 \text{ per cent.}$$

Solving for $x$: $x = \dfrac{1.00}{1.0 \times 0.0691 \times 100} = \dfrac{1.00}{6.91} = 0.1447$, the normality of the acid solution required.

# CHAPTER XIX

## PROBLEMS

**1.** Calculate the percentages of K and $K_2O$ in $K_2SO_4$.
**2.** Calculate the percentages of CaO and $SiO_2$ in $CaSiO_3$.
**3.** Calculate the percentages of Fe and FeO in $Fe_2O_3$.
**4.** Calculate the percentages of ZnO and $P_2O_5$ in $Zn_2P_2O_7$.
**5.** Calculate the chemical factors for:

- a. Cl in AgCl.
- b. Ca in $CaSO_4$.
- c. As in $As_2O_3$.
- d. $SO_2$ in $BaSO_4$.
- e. Pb in $PbCrO_4$.
- f. MgO in $Mg_2P_2O_7$.

**6.** Calculate the chemical factors for:

- a. $NH_3$ in $(NH_4)_2PtCl_6$.
- b. $P_2O_5$ in $Mg_2P_2O_7$.
- c. C in $CO_2$.
- d. Al in $Al_2O_3$.
- e. Cu in $Cu_2O$.
- f. Fe in $Fe_2O_3$.

**7.** How many grams of silver must be dissolved in nitric acid in order to obtain 100.0 grams of silver nitrate?

**8.** A precipitate of 2.600 grams of $BaSO_4$ was obtained by precipitation of the soluble sulfur in a sample of mineral. How many grams of sulfur were present in the mineral?

**9.** The $CaCO_3$ in a sample of limestone gave a precipitate of 2.506 grams of $CaC_2O_4$. What weight of $CaCO_3$ is represented in the precipitate?

**10.** Calculate the weight of $MgNH_4PO_4$ which upon ignition will give 0.7506 gram of $Mg_2P_2O_7$.

**11.** A sample of limestone containing 15.00 per cent $MgCO_3$ on being analyzed gave 0.2064 gram of $Mg_2P_2O_7$. Calculate the weight of the sample used.

**12.** An ammonium sulfate fertilizer upon treatment with NaOH yielded $NH_3$ which was precipitated as $(NH_4)_2PtCl_6$. Upon ignition of the latter, a residue of 0.1200 gram of Pt remained. Calculate the weight of N present in the fertilizer.

**13.** A piece of silver alloy weighing 0.1500 gram was dissolved in acid and the silver precipitated as AgCl. If a precipitate of 0.1607 gram of AgCl was obtained, calculate the percentage of silver in the alloy.

**14.** Calculate the number of ml. of $AgNO_3$ solution (10.00 gms. $AgNO_3$ per 100 ml. of solution) required to completely precipitate the Cl from 0.2505 gram of $BaCl_2 \cdot 2\ H_2O$.

**15.** Calculate the number of ml. of $NH_4Cl$ solution (26.80 grams $NH_4Cl$ per liter) required to completely precipitate 0.4505 gram of Ag from solution.

**16.** Assume a sample received to be pure $Na_2SO_4$. Calculate the weight of sample required so that all the sulfur present will be precipitated by 55.00 ml. of a $BaCl_2 \cdot 2\ H_2O$ solution (12.05 grams of $BaCl_2 \cdot 2\ H_2O$ per 100 ml.).

**17.** Calculate the Sp. Gr.$^{25^\circ}_{25^\circ}$ of a solution from the following data: Weight of dry pycnometer, 15.24 grams; weight of pycnometer plus water at 25° C., 40.02 grams; weight of pycnomter plus solution at 25° C., 45.38 grams.

**18.** Calculate the Sp. Gr.$^{20^\circ}_{4^\circ}$ of a liquid from the following data: Weight of dry pycnometer, 20.08 grams; weight of pycnometer plus water at 20° C., 44.96 grams; weight of pycnometer plus liquid at 20° C., 42.12 grams; density of water at 20° C., 0.9982.

**19.** Calculate the number of ml. of $NH_4OH$ solution (Sp. Gr. 0.9580 and containing 10.47 per cent $NH_3$ by weight) required to completely precipitate the Fe in solution from a 3.714 gram sample containing 35.00 per cent by weight of $FeCl_3$.

**20.** Calculate the number of ml. of hydrochloric acid (Sp. Gr. 1.075 and containing 15.16 per cent of HCl) required to dissolve 1.200 grams of calcium carbonate.

**21.** A 1.204 gram sample of barium carbonate containing 5.50 per cent $SiO_2$ as an impurity is dissolved in acid. Calculate the ml. of sulfuric acid solution (Sp. Gr. 1.185 containing 25.40 per cent $H_2SO_4$) required to completely precipitate the Ba as $BaSO_4$.

**22.** Calculate the number of ml. of hydrochloric acid (Sp. Gr. 1.100 and containing 20.01 per cent of HCl) required to completely precipitate the silver from a solution containing 0.6540 gram of silver nitrate.

**23.** A 2.000 gram sample of an air-dry feed upon ignition gave a residue of 0.0462 gram of ash. Calculate the percentage of ash in the air-dry feed.

**24.** 100.0 grams of freshly harvested grain after exposure to air for several weeks weighed 85.06 grams. A 2.000 gram sample of this air-dried grain after drying in a moisture oven weighed 1.880 grams. What was the percentage of moisture in the freshly harvested grain?

**25.** Calculate the percentage by weight of methyl alcohol in an alcohol-water solution from the following data: Pure methyl alcohol at 15° C. has a Sp. Gr. of 0.7958 and water at the same temperature has a Sp. Gr. of 0.9991. The alcohol-water solution has a Sp. Gr. of 0.8655 and is an 80.48 per cent alcohol solution by volume.

**26.** If 654.0 ml. of 95.00 per cent by weight ethyl alcohol solution (Sp. Gr. at 25° C. of 0.7997) is mixed with 976.0 ml. of water (Sp. Gr. at 25° C. of 0.9971), calculate the percentage by weight of ethyl alcohol in the mixed solution.

**27.** Calculate the milliequivalent weight in grams (weight contained in 1 ml. of a normal solution) of the following substances used in acidimetry and alkalimetry:

a. $Na_2CO_3$
b. $K_2O$
c. $NH_4OH$
d. $Ba(OH)_2$
e. $H_3PO_4$
f. $HNO_3$
g. succinic acid
h. sulfamic acid

**28.** Calculate the ml. of HCl (Sp. Gr. 1.195 containing 38.16 per cent HCl) required to prepare a liter of N/14 solution.

**29.** Calculate the grams of KOH required to prepare 5 liters of 0.1205 N solution.

**30.** Calculate the grams of crystallized oxalic acid ($H_2C_2O_4 \cdot 2\ H_2O$) required to prepare a liter of 0.2000 N solution.

**31.** To an aqueous solution of 0.2126 gram of pure $Na_2CO_3$ were added 50.00 ml. of a sulfuric acid solution, the solution boiled to expel the $CO_2$, and, after cooling, the excess acid was titrated with 4.75 ml. of a sodium hydroxide solution. 1.00 ml. of the sulfuric acid solution is equivalent to 0.9520 ml. of the sodium hydroxide solution. Calculate the normal factor of the sulfuric acid solution and of the sodium hydroxide solution.

**32.** 0.1872 gram of pure $Na_2CO_3$ was dissolved in 35.00 ml. of a sulfuric acid solution. The solution was boiled to expel the $CO_2$ and, when cool, titrated with 7.60 ml. of a potassium hydroxide solution. 20.00 ml. of the potassium hydroxide solution are neutralized by 18.90 ml. of the sulfuric acid solution. Calculate the normal factors of the sulfuric acid and potassium hydroxide solutions.

**33.** Calculate the $K_2O$-titer, the $CaCO_3$-titer, and the NaOH-titer of a 0.1500 N sulfuric acid solution.

**34.** Calculate the ml. of $NH_4OH$ (Sp. Gr. 0.882 and containing 34.95 per cent of $NH_3$) required to prepare 1 liter of 0.1000 N solution.

**35.** Calculate the ml. of $H_2SO_4$ (Sp. Gr. 1.840 and containing 98.72 per cent $H_2SO_4$) required to prepare 500.0 ml. of a 0.0714 N solution.

**36.** Calculate the normal factor of a solution made by diluting 252.0 ml. of hydrochloric acid (Sp. Gr. 1.100 and containing 20.01 per cent HCl) to 1500 ml. with water.

**37.** Calculate the normal factor of a solution made by dissolving and diluting 24.02 gm. of NaOH to 500 ml. with water.

**38.** Calculate the normal factor of an acid solution if 10.00 ml. of the acid solution are neutralized by 12.10 ml. of 0.0975 N alkali solution.

**39.** Calculate the normal facor of an alkali solution, 25.00 ml. of which are equivalent to 23.50 ml. of an N/14 acid solution.

**40.** Calculate the normal factor of an acid solution, 20.00 ml. of which are equivalent to 11.40 ml. of a sodium carbonate solution (containing 5.300 grams of $Na_2CO_3$ per 500 ml. of solution).

**41.** 20.00 ml. of a standard hydrochloric acid solution were diluted to 200.0 ml. A 20.00 ml. aliquot of this solution upon treatment with silver nitrate yielded a precipitate of 0.3604 gram of silver chloride. Calculate the normal factor of the standard hydrochloric acid solution.

**42.** 25.00 ml. of a standard sulfuric acid solution were treated with barium chloride solution yielding a precipitate of 0.9800 gram of barium sulfate. What is the normal factor of the standard acid solution?

**43.** 25.00 ml. of a standard hydrochloric acid solution are found to be equivalent to 26.20 ml. of an 0.6284 N alkali solution. Calculate the grams of silver chloride precipitate that should be obtained if 10.00 ml. of the standard acid solution are treated with silver nitrate.

**44.** 49.70 ml. of ammonium hydroxide solution (Sp. Gr. 0.9440) were diluted to 500.0 ml. If 57.00 ml. of this solution are equivalent to 45.40 ml. of 0.5000 N acid solution, what is the percentage of $NH_3$ in the original ammonium hydroxide solution.

**45.** Calculate the percentage of HCl in a 7.300 N hydrochloric acid solution with a Sp. Gr. of 1.120.

**46.** 25.00 ml. of sulfuric acid (Sp. Gr. 1.840) were diluted to 500.0 ml. with water. 20.00 ml. of the diluted acid were found to be equivalent to 35.90 ml. of N alkali solution. Calculate the percentage of $H_2SO_4$ by weight in the undiluted sulfuric acid sample.

**47.** How many grams of hydrochloric acid must be contained in 1 liter of solution so that 1.00 ml. of the solution will neutralize 0.045 gram of potassium hydroxide?

**48.** Calculate the ml. of water necessary to add to 1 liter of 0.1500 N sulfuric acid in order to make it exactly N/14.

**49.** 5.000 grams of a mixture containing sodium hydroxide and sodium carbonate are dissolved in water and diluted to 250.0 ml. A 25.00 ml. aliquot of this solution required 16.20 ml. of 0.5000 N acid with phenolphthalein as an indicator, and 20.40 ml. of 0.5000 N acid with methyl orange as an indicator. Calculate the percentage of sodium hydroxide and sodium carbonate present in the sample.

**50.** Calculate the weight of pure sodium carbonate to be dissolved and diluted to 500.0 ml. so that 25.00 ml. of the sodium carbonate solution will be equivalent to 25.00 ml. of an N/5 acid solution.

**51.** In standardizing an approximately N/14 sodium hydroxide solution, benzoic acid ($C_6H_5COOH$) is used as a primary standard. Assuming the sodium hydroxide solution to be exactly N/14, how many grams of benzoic acid must be weighed out so that 25.00 ml. of the sodium hydroxide solution will be neutralized in the titration.

**52.** Calculate the percentage strength of a sodium hydroxide solution so that 200.0 ml. of it when added to 200.0 ml. of a 1.25 per cent sulfuric acid solution will give a final solution of 1.25 per cent sodium hydroxide. Assume the specific gravities of both solutions to be 1.000 and that no contraction or expansion in volume occurs when the two solutions are mixed.

**53.** What weight in grams of soda ash must be taken for analysis in order that each ml. of 0.2000 N hydrochloric acid used in the titration will represent 1.00 per cent of sodium carbonate?

**54.** Calculate the grams of acetic acid present per 100.0 ml. of vinegar if a 5.00 ml. sample of the vinegar, diluted to 50 ml. with water, required 44.83 ml. of 0.0970 N sodium hydroxide solution for neutralization.

**55.** Calculate the percentage of acetic acid in a vinegar with a specific gravity of 1.012, if a 5.00 ml. sample required 35.60 ml. of 0.1012 N sodium hydroxide solution for neutralization.

**56.** Calculate the grams of acetic acid present in 100.0 ml. of vinegar if a 5.00 ml. sample of the vinegar diluted with 50.00 ml. of water required 32.5 ml. of a sodium hydroxide solution for neutralization. The sodium hydroxide solution has an acetic acid-titer of 0.0081.

**57.** Calculate the milliequivalent weight in grams (weight contained in 1 ml. of a normal solution) of the following substances used in oxidation and reduction reactions.

a. $K_2Cr_2O_7$
b. $FeSO_4 \cdot 7H_2O$
c. $KIO_3$
d. $H_2O_2$
e. $CuO$
f. $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$
g. $As_2O_5$
h. $H_3AsO_3$
i. $Na_2S_2O_3$
j. $Cu_2O$

**58.** Calculate the grams of potassium permanganate required to make 500.0 ml. solutions of the following normalities: 0.15 N; 1.5 N; and N/14. Do the same for potassium dichromate.

**59.** 0.4000 gram of pure sodium oxalate, dissolved in sulfuric acid solution, reduced 26.50 ml. of a potassium permanganate solution. Calculate the normal factor of the potassium permanganate solution.

**60.** 0.1000 gram of iron wire (99.90 per cent pure Fe) was dissolved in sulfuric acid out of contact with air and titrated with 0.0950 N potassium permanganate solution. Calculate the number of ml. of permanganate solution used in the titration.

**61.** Calculate the grams of avilable oxygen in 1.00 ml. of a potassium permanganate solution, 10.80 ml. of which are equivalent to 0.1000 gram of pure iron.

**62.** If 1.00 ml. of a potassium permanganate solution contains 0.0054 gram of available oxygen, what is the normal factor of the solution?

**63.** 2.000 grams of ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$) were dissolved and diluted to a 200.0 ml. volume. 25.00 ml. of this solution were oxidized by 22.50 ml. of a standard potassium permanganate solution. 20.00 ml. of the standard potassium permanganate solution are equivalent to 0.1674 gram of iron. Calculate the percentage purity of the ammonium oxalate.

**64.** Calculate the milliliters of 0.1206 N $KMnO_4$ solution required to add to a liter of 0.0754 N $KMnO_4$ solution to make an exactly 0.1 N $KMnO_4$ solution.

**65.** Calculate the grams of $Na_2C_2O_4$ that should be weighed as a primary standard to react with 30.00 ml. of a 0.1500 N $KMnO_4$ solution.

**66.** If a $H_2C_2O_4 \cdot 2H_2O$ solution is 0.1000 N when used as an acid, what is its normality when used as a reducing agent with $KMnO_4$ in acid solution.

**67.** 0.1033 gram of crystalline oxalic acid which had been heated and had lost some of its water of crystallization was dissolved in water and titrated with 20.50 ml. of 0.1000 N potassium permanganate solution. What percentage of the water of crystallization had been lost? Crystalline oxalic acid has the formula $H_2C_2O_4 \cdot 2H_2O$.

**68.** 1.500 grams of a substance containing calcium were dissolved and diluted to 500.0 ml. The calcium was precipitated from a 50.00 ml. aliquot of this solution as calcium oxalate, dissolved in dilute sulfuric acid and titrated with 25.40 ml. of standard potassium permanagnate solution. 10.00 ml. of the standard potassium permanganate solution are equivalent to 0.0710 gram of sodium oxalate. Calculate the percentage of calcium in the sample.

69. Calculate the grams of each of the following reducing agents required to make a liter of 0.1000 N solution: $H_2C_2O_4 \cdot 2H_2O$; $FeSO_4 \cdot 7H_2O$; and $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$.

70. Calculate the Fe-titer; the FeO-titer; and the $Fe_2O_3$-titer of a 0.1 N $KMnO_4$ solution.

71. Calculate the normal factor of a $KMnO_4$ solution where 1 ml. of the solution is equivalent to 0.001 gram of Fe; 0.001 gram FeO.

72. The Fe-titer of a $KMnO_4$ solution is 0.0075. What is the normal factor of the solution?

73. A 0.2840 gram sample of iron ore was dissolved in hydrochloric acid and the iron reduced to the ferrous state. 21.20 ml. of $KMnO_4$ solution with a Fe-titer of 0.0072 were required to titrate the ferrous iron. Calculate the percentage of Fe and FeO in the sample.

74. A 0.3000 gram sample of iron ore was dissolved in acid and the iron reduced to the ferrous state. The following volumes of solutions were used to titrate the ferrous solution in an acid medium: 38.40 ml. of 0.1025 N $KMnO_4$ solution; 1.95 ml. of $FeSO_4$ solution. 1.00 ml. of $KMnO_4 \approx 0.95$ ml. of $FeSO_4$. Calculate the percentage of iron in the ore.

75. Calculate the normal factor required for a $KMnO_4$ solution so that when a 1.000 gram iron-containing sample is analyzed, the milliliters of $KMnO_4$ solution used for titration will be numerically equal to the percentage of Fe in the sample.

76. Determine the milliliters of 0.7500 N $KMnO_4$ solution which will react with 10.00 ml. of a 3.00 per cent $H_2O_2$ solution with a specific gravity of 1.010.

77. 10.00 ml. of an $H_2O_2$ solution with a specific gravity of 1.000 were diluted to 100 ml., and a 10.00 ml. aliquot acidified with sulfuric acid required 17.20 ml. of 0.0931 N $KMnO_4$ solution for titration. Calculate the percentage by weight of the $H_2O_2$ in the original peroxide solution.

78. Ferrous sulfate reduces $MnO_2$ according to the following equation:

$$2\,FeSO_4 \cdot 7\,H_2O + MnO_2 + H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 16\,H_2O$$

Calculate the number of milliliters of 0.1520 N $FeSO_4 \cdot 7\,H_2O$ solution required to reduce 0.2000 gram of $MnO_2$.

79. A 0.3000 gram sample of $MnO_2$ ore (pyrolusite) was treated with 50.00 ml. of 0.1050 N ferrous sulfate solution. The excess ferrous sulfate was back-titrated with 9.55 ml. of 0.1150 N $KMnO_4$ solution. Calculate the percentage of $MnO_2$ in the ore.

80. A piece of pure iron wire weighing 0.2441 gram is dissolved in hydrochloric acid, reduced to $FeCl_2$ by $SnCl_2$, and titrated with 27.35 ml. of a $K_2Cr_2O_7$ solution. Calculate the normal factor of the $K_2Cr_2O_7$ solution.

81. Calculate the normal factor of a $FeSO_4 \cdot 7H_2O$ solution if 25.00 ml. of the ferrous sulfate solution are equivalent to 21.40 ml. of a standard $K_2Cr_2O_7$ solution. A 20.00 ml. volume of the $K_2Cr_2O_7$ solution will oxidize 0.1340 gram of pure iron when dissolved in HCl and reduced to $FeCl_2$.

**82.** A 0.3000 gram sample of iron ore was dissolved in hydrochloric acid, the iron reduced by stannous chloride, and then titrated with 20.80 ml. of 0.1545 N $K_2Cr_2O_7$ solution. Calculate the per cent of Fe and of FeO in the iron-ore sample.

**83.** Pure iron wire weighing 0.2164 gram was dissolved in hydrochloric acid, reduced to $FeCl_2$ by $SnCl_2$, and titrated with 30.70 ml. of a ceric sulfate solution. Calculate the normal factor of the ceric sulfate solution.

**84.** A 0.2865 gram sample of iron ore was dissolved in hydrochloric acid and the iron, after reduction by stannous chloride, titrated with 21.92 ml. of 0.1053 N ceric sulfate solution. Calculate the percentage of Fe and FeO in the iron ore sample.

**85.** Calculate the weight in grams of pure $As_2O_3$ to be used as a primary standard to react with 20.00 ml. of 0.1375 N iodine solution.

**86.** 0.2000 gram $As_2O_3$ is dissolved and oxidized by 20.20 ml. of standard iodine solution. 10.00 ml. of the standard iodine solution are equivalent to 12.50 ml. of sodium thiosulfate solution. Calculate the normal factor of the thiosulfate solution.

**87.** 3.000 grams of arsenious oxide were dissolved and diluted to a volume of 500.0 ml. 25.00 ml. of this solution were titrated with 35.50 ml. of an iodine solution. Calculate the grams of iodine in 1.00 ml. of the iodine solution.

**88.** Cupric salts in solution with potassium iodide liberate an equivalent amount of iodine according to the equation:

$$2\,Cu(C_2H_3O_2)_2 + 4\,KI = Cu_2I_2 + I_2 + 4\,KC_2H_3O_2$$

Calculate the grams of copper which will furnish enough iodine to react with 25.00 ml. of 0.1 N sodium thiosulfate solution.

**89.** Crystallized sodium thiosulfate ($Na_2S_2O_3 \cdot 5\,H_2O$) on standing in air lost some of its water of crystallization. 1.240 grams were dissolved in water and titrated with 11.20 ml. of an iodine solution (1.00 ml. of which is equivalent to 0.0245 gram of $As_2O_3$). Calculate the percentage of the water of crystallization which was lost.

**90.** If 22.00 ml. of a standard iodine solution will oxidize 0.1000 gram of arsenious oxide to the arsenic oxide, what must be the normal factor of a potassium permanganate solution so that 20.00 ml. of the potassium permanganate solution will liberate the 22.00 ml. of standard iodine solution from a potassium iodide solution containing acetic acid.

**91.** What will be the normal factor of an iodine solution resulting when 100.0 ml. of 0.2464 N potassium permanganate solution is treated with 12.1 grams of potassium iodide and diluted to 200.0 ml. with an acetic acid solution?

**92.** A 0.2000 gram sample of impure $Na_2SO_3$ is dissolved and titrated with 32.15 ml. of a standard iodine solution. 1.00 ml. of the standard iodine solution is equivalent to 0.0116 gram iodine. Calculate the percentage purity of the $Na_2SO_3$.

**93.** Exactly 10.00 ml. of a $H_2O_2$ solution with a specific gravity of 1.010 were treated with excess KI in sulfuric acid solution, and the iodine liberated titrated with 29.10 ml. of 0.5842 N $Na_2S_2O_3$ solution. Calculate the percentage strength of the $H_2O_2$ solution.

**94.** Calculate the milliequivalent weight in grams (weight contained in 1 ml. of a normal solution) of the following substances used in volumetric precipitation reactions:

a. NaCl
b. $AgNO_3$
c. NaCNS
d. $NH_4CNS$
e. $BaCl_2 \cdot 2\ H_2O$
f. $Cl^-$

**95.** Calculate the normal factor of a silver nitrate solution from the following data: 5.000 grams of pure KCl were dissolved and diluted to a 500.0 ml. volume. A 25.00 ml. aliquot of this solution required 35.60 ml. of a silver nitrate solution for complete precipitation of the chloride.

**96.** A 25.00 ml. volume of a 0.1073 N $AgNO_3$ solution was titrated with 26.25 ml. of a KCNS solution. Calculate the normal factor of the KCNS solution. What is the Cl-titer of the $AgNO_3$ solution?

**97.** A 5.000 gram sample of hamburger was treated with 50.00 ml. of $AgNO_3$ solution having a NaCl-titer of 0.005583, digested with $HNO_3$ and $KMnO_4$ to remove organic matter, and after the addition of 10 ml. of acetone, required 39.10 ml. of a KCNS solution for back titration of the excess $AgNO_3$. 1.00 ml. $AgNO_3 \approx$ 1.15 ml. of KCNS. Calculate the percentage of NaCl in the hamburger.

**98.** A 2 ml. portion of a sodium chloride solution is added to 3.00 grams of cheese. Exactly 50.00 ml. of 0.1095 N $AgNO_3$ solution are added, the organic matter destroyed by wet ashing, and the excess $AgNO_3$ titrated with 11.45 ml. of 0.1050 N KCNS solution. A 3.000 gram sample of the cheese (control sample) was treated with 50.00 ml. of the standard $AgNO_3$ solution, digested, and the excess $AgNO_3$ titrated with 40.30 ml. of the standard KCNS solution. Calculate the milligrams of NaCl added to the cheese and the milligrams of NaCl present per gram of the original cheese.

**99.** 100.0 grams of freshly harvested grain upon drying in air for several weeks were found to weigh 80.25 grams. A 2.000 gram sample of the air-dried grain upon drying to constant weight in a 100° C. moisture oven weighed 1.750 grams. Calculate the percentage of moisture in the freshly harvested grain.

**100.** A 2.468 gram sample of feed on drying to constant weight at 100° C. weighed 2.244 grams. This dried sample was extracted with ether, giving an ether extract of 0.1520 gram. Calculate the percentage of ether extract on the original moisture basis, on a moisture-free basis and on a 15 per cent moisture basis.

**101.** 150.0 grams of freshly harvested grain upon air-drying weighs 130.0 grams. A 2.000 gram sample of the air-dry feed upon further drying at 100° C. weighs 1.900 grams. This sample upon ether extraction and reweighing weighs 1.802 grams. Calculate the percentage of ether extract on the air-dry basis, and on a 13.5 per cent moisture basis.

**102.** A 2.563 gram sample of air-dry feed with a 14.50 per cent moisture content was analyzed for crude fiber. Weight of the crucible, 10.0505 grams. Weight of the crucible plus dry fiber, 10.2000 grams. Weight of the crucible and contents after ashing, 10.1000 grams. Calculate the percentage of crude fiber on the air-dry and on a 9.0 per cent moisture basis.

**103.** A 1.500 gram sample of air-dry feed containing 8.25 per cent moisture was analyzed for protein content by the Kjeldahl method. The ammonia was absorbed in 25.00 ml. of 0.4950 N hydrochloric acid. The excess acid in the receiving flask was neutralized with 12.00 ml. of standard sodium hydroxide solution (21.20 ml. of NaOH solution equivalent to 18.00 ml. of N/2 HCl solution). Calculate the percentage of total protein in the sample using 6.25 as the factor for converting N to protein. Also calculate the percentage protein on a 15.00 per cent moisture basis.

**104.** A feed contains 23.00 per cent of protein on a 15 per cent moisture basis. This feed, on standing, lost moisture so that it contained only 13.5 per cent moisture. A 2.000 gram sample of this partially dried feed was then analyzed for protein by the Kjeldahl method. Calculate the ml. of 0.1 N acid required in the receiving flask to neutralize all the ammonia obtained upon distillation.

**105.** A sample of silage is allowed to dry in air and loses 91.61 per cent moisture. On further drying at 100° C., the air-dry material is found to contain 0.94 per cent of moisture. If the air-dry material contains 13.28 per cent protein, what is the protein percentage of the original fresh silage?

**106.** A feedstuff on a 12 00 per cent moisture basis is guaranteed to contain 18.00 per cent protein. If a 2.000 gram sample, when analyzed for protein by the Kjeldahl method, contained 15.00 per cent moisture, calculate the ml. of N/14 acid to put in the receiving flask to exactly neutralize all the $NH_3$ distilled.

**107.** In a protein determination on a feedstuff, using the Kjeldahl method, the ammonia is distilled into a saturated boric acid solution and titrated with a standard acid solution. (a) Calculate the normal factor of the standard acid solution, so that, if a 1.000 gram sample of the feedstuff is analyzed, each milliliter of standard acid used in the titration will be numerically equal to 0.1 per cent nitrogen. (b) Calculate the normal factor of the standard acid solution so that, if a 1.000 gram sample of feedstuff is analyzed, the milliliters of standard acid used in the titration will be numerically equal to the percentage protein. Use the factor 6.25 to convert nitrogen to protein.

**108.** Calculate the mg. of $Cu_2O$ obtained in the reaction between a reducing sugar solution and Fehling's solution according to the Munson and Walker method. The copper precipitate was filtered, washed and then dissolved in 20.00 ml. of ferric alum solution (approximately 20 per cent $Fe_2(SO_4)_3(NH_4)_2(SO_4)_2$ in a 20 per cent sulfuric acid solution) and titrated with 30.00 ml. of a standard potassium permanganate solution. 1.00 ml. of the potassium permanganate solution in the presence of acid will deliver 0.00075 gram of oxygen.

**109.** Exactly 8.000 grams of maple sugar (mostly sucrose with a small amount of invert sugar) were dissolved and diluted to 100.0 ml. A 25.00 ml. aliquot was analyzed for invert sugar by the Munson and Walker copper reduction method, and gave 0.1515 gram of $Cu_2O$ precipitate. Using the Munson and Walker table on pages 165–170, calculate the percentage of invert sugar present in the sample.

**110.** A 2.500 gram sample of impure dextrose was dissolved and diluted to 250.0 ml. of solution. A 25.00 ml. aliquot was analyzed by the Quisumbing and Thomas copper reduction method. The reduced copper was converted to copper acetate, and, after the addition of potassium iodide, was titrated with 36.27 ml. of 0.1545 N sodium thiosulfate solution. Using the Quisumbing and Thomas table on page 173, calculate the per cent dextrose in the sample.

**111.** The starch in a 2.000 gram sample of material was hydrolyzed to dextrose, dissolved, and diluted to a 250.0 ml. volume. A 25.00 ml. aliquot of the solution was analyzed by the Munson and Walker method. The reduced copper was treated with ferric sulfate-sulfuric acid solution, and the ferrous sulfate produced titrated with 27.77 ml. of a 0.2052 N potassium permanganate solution. Using Hammond's table on page 174, and the factor 0.90 to convert dextrose to starch, calculate the percentage starch in the sample.

**112.** A 1.000 gram sample of impure lactose was dissolved and diluted to 1 liter in volume. 1.00 ml. of this solution was analyzed by the Folin-Wu sugar method. The colored solution obtained was compared in a visual colorimeter with a standard solution obtained by treating 1.00 ml. of a solution containing 1.00 mg. lactose exactly as the sample. The color intensity of the standard tube set at 20.0 was matched by the sample tube set at 22.5 on the colorimeter. Using Beer's law, calculate the per cent lactose in the impure sample.

**113.** 52.00 grams of maple sirup were treated with a clarifying agent, diluted to 200.0 ml. volume, and filtered. Invert sugar was determined on a 25.00 ml. aliquot of the filtrate by the Munson and Walker method and a precipitate of 0.2145 gram of $Cu_2O$ obtained. Calculate the percentage of invert sugar present in the sample with the aid of the Munson and Walker table (pp. 165–170).

**114.** Calculate the Winton lead number (p. 245) for a maple sirup sample from the following data: Weight of sirup sample, 25.15 grams; 25.00 ml. of basic lead acetate solution added to the sample and to a blank; the sample and blank diluted to a volume of 100.0 ml., 10.00 ml. aliquots removed from each, and the lead precipitated as $PbSO_4$ and weighed; $PbSO_4$ from the blank weighed 0.1950 gram, from the sample weighed 0.1458 gram.

**115.** A 4.555 gram fat sample was saponified by heating with 50.00 ml. of an alcoholic potassium hydroxide solution. The excess alkali in the sample after saponification required 29.90 ml. of 0.5642 N acid for neutralization. (A blank determination employing 25.00 ml. of the alcoholic potassium hydroxide solution required 30.80 ml. of 0.5642 N acid for titration.) Calculate the saponification number of the fat.

**116.** A 5.000 gram sample of fat containing 2.50 per cent of non-saponifiable matter was saponified by heating with 50.00 ml. of alcoholic potassium hydroxide solution. A volume of 37.60 ml. of 0.5242 N acid were required to back titrate the excess alkali. A blank determination employing 25.00 ml. of the alcoholic potassium hydroxide solution required 32.84 ml. of the 0.5242 N acid for titration. Calculate the saponification number of the fat sample. Calculate the saponification number of the fat after removal of the non-saponifiable matter.

**117.** A 10.58 gram sample of fat was treated with 50 ml. of alcohol and the free fatty acids present titrated with 4.50 ml. of 0.0714 N alkali. A blank determination on 50 ml. of the alcohol required 0.25 ml. of the standard alkali solution for titration. Calculate the free fatty acid number of the fat.

**118.** A 0.2021 gram sample of a liquid fat was treated with 25.00 ml. of Wiji iodine solution. After standing 30 min., the excess halogen was back titrated with 21.10 ml. of 0.1075 N sodium thiosulfate solution. A blank determination employing 25.00 ml. of the Wiji iodine solution required 37.20 ml. of the standard thiosulfate solution for titration. Calculate the iodine number of the fat.

**119.** Calculate the Reichert-Meissl number for a butter fat (p. 232) from the following data: 5.194 gram sample; 110.0 ml. of distillate collected; 100.0 ml. aliquot of the filtered distillate required 26.2 ml. of 0.1052 N sodium hydroxide solution for neutralization.

**120.** Calculate the Polenske number for a butter fat (p. 232) from the following data: 4.984 gram sample; the volatile insoluble acids obtained from 110.0 ml. of distillate required 2.60 ml. of 0.0982 N sodium hydroxide solution for neutralization.

**121.** Calculate the percentage of fat adulterant present in butter fat (p. 234) and name the type of adulterant from the following data on two butter samples:

a. Reichert-Meissl number 16.20; Polenske number 1.7.
b. Reichert-Meissl number 14.60; Polenske number 11.2.

**122.** In the nitrogen determination on fertilizers, the procedure calls for a sample weight of 0.4–3.5 grams, depending upon the nitrogen content of the fertilizer. If a commercial sample of potassium nitrate were being analyzed, what weight sample should be taken if 50.0 ml. of 0.1 N acid are used in the receiving flask to collect all the nitrogen distilled as ammonia-nitrogen.

**123.** A 0.6100 gram sample of nitrate-containing fertilizer was analyzed by the modified Kjeldahl method to include the nitrogen of nitrates; 50.00 ml. of 0.1012 N acid were placed in the receiving flasks for the sample and the blank; 49.80 ml. of 0.1010 N alkali were required for back titration of the blank, and 15.30 ml. for the sample. Calculate the percentage of nitrogen and nitrate-nitrogen in the fertilizer sample.

**124.** A 2.500 gram sample of a fertilizer containing phosphorus was digested, diluted to 250.0 ml. volume, and filtered. The phosphorus was precipitated in a 50.00 ml. aliquot of the solution as ammonium phosphomolybdate, dissolved, and re-precipitated as magnesium ammonium phosphate. Upon ignition, 0.1400 gram of magnesium pyrophosphate ($Mg_2P_2O_7$) was obtained. Calculate the percentage of phosphorus and $P_2O_5$ in the sample.

**125.** A 0.5000 gram sample of a phosphorus-containing fertilizer was digested, diluted to 500.0 ml., and filtered. The phosphorus in a 50.00 ml. aliquot of the solution was precipitated as the ammonium phosphomolybdate. The precipitate was washed and then dissolved in 30.00 ml. of 0.3300 N sodium hydroxide solution. The excess alkali was neutralized by 10.00 ml. of 0.1500 N acid solution using phenolphthalein as indicator. Calculate the percentage of P and $P_2O_5$ in the fertilizer sample.

**126.** A 1.500 gram sample of a potassium-containing fertilizer is ashed, dissolved, diluted to a 500.0 ml. volume, and filtered. The potassium is precipitated in a 50.00 ml. aliquot of this solution as potassium chloroplatinate ($K_2PtCl_6$), yielding a precipitate of 0.1858 gram. Calculate the percentage of K and $K_2O$ in the fertilizer sample.

**127.** The calcium in a 0.7342 gram sample of limestone was precipitated as calcium oxalate. Upon ignition, 0.3979 gram of CaO was obtained. Calculate the percentage of Ca, CaO, and $CaCO_3$ in the sample.

**128.** The magnesium present in a 0.6842 gram sample of limestone yielded a precipitate of 0.4441 gram of $Mg_2P_2O_7$. Calculate the percentage of Mg, MgO, and $MgCO_3$ in the sample.

**129.** A 1.204 gram sample of limestone was treated with 50.00 ml. of 0.4805 N nitric acid. The excess acid was back titrated with 35.80 ml. of 0.2506 N sodium hydroxide solution. Calculate the neutralizing value of the limestone in percentage of calcium carbonate.

**130.** What weight in grams of limestone must be taken for analysis for each milligram of calcium sulfate to represent 0.10 per cent of CaO?

**131.** 1.850 grams of lead arsenate are analyzed for total arsenic by the cuprous chloride distillation method. The $AsCl_3$ solution obtained is diluted to a liter and a 200.0 ml. aliquot titrated with 0.1025 N iodine solution, 40.50 ml. being used. Calculate the percentage of $As_2O_5$ and the percentage of As present in the sample.

**132.** Dissolve 0.6000 gram of lead arsenate in hydrochloric acid and, after the addition of potassium iodide, titrate the liberated iodine with standard sodium thiosulfate solution. If 44.00 ml. of 0.1500 N sodium thiosulfate were used, calculate the percentage of $As_2O_5$ present in the sample.

**133.** A 0.5000 gram sample of insecticide containing lead was dissolved and the lead precipitated as lead chromate. A precipitate of 0.4500 gram of lead chromate was obtained. Calculate the percentage of lead oxide (PbO) present in the sample.

**134.** A 0.8000 gram sample of Paris green was treated with $CuCl_2$ and hydrochloric acid, the arsenic being converted to $AsCl_3$ and distilled into water. The distillate was diluted to a volume of 1 liter, a 200.0 ml. aliquot removed, neutralized with sodium bicarbonate, and titrated with 18.00 ml. of 0.0990 N iodine solution. Calculate the percentage of As present in the Paris green sample.

**135.** The copper in a 2.200 gram sample of Paris green was precipitated as $Cu(OH)_2$, dissolved in acid, and diluted to a 250.0 ml. volume. A 100.0 ml. aliquot of the solution upon subsequent treatment with excess KI, required 26.20 ml. of 0.1242 N sodium thiosulfate solution to titrate the liberated iodine. Calculate the percentage of Cu and CuO in the sample.

## TABLE 25. FOUR PLACE LOGARITHMS

| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **10** | 0000 | 0043 | 0086 | 0128 | 0170 | 0212 | 0253 | 0294 | 0334 | 0374 | 4 | 8 | 12 | 17 | 21 | 25 | 29 | 33 | 37 |
| 11 | 0414 | 0453 | 0492 | 0531 | 0569 | 0607 | 0645 | 0682 | 0719 | 0755 | 4 | 8 | 11 | 15 | 19 | 23 | 26 | 30 | 34 |
| 12 | 0792 | 0828 | 0864 | 0899 | 0934 | 0969 | 1004 | 1038 | 1072 | 1106 | 3 | 7 | 10 | 14 | 17 | 21 | 24 | 28 | 31 |
| 13 | 1139 | 1173 | 1206 | 1239 | 1271 | 1303 | 1335 | 1367 | 1399 | 1430 | 3 | 6 | 10 | 13 | 16 | 19 | 23 | 26 | 29 |
| 14 | 1461 | 1492 | 1523 | 1553 | 1584 | 1614 | 1644 | 1673 | 1703 | 1732 | 3 | 6 | 9 | 12 | 15 | 18 | 21 | 24 | 27 |
| 15 | 1761 | 1790 | 1818 | 1847 | 1875 | 1903 | 1931 | 1959 | 1987 | 2014 | 3 | 6 | 8 | 11 | 14 | 17 | 20 | 22 | 25 |
| 16 | 2041 | 2068 | 2095 | 2122 | 2148 | 2175 | 2201 | 2227 | 2253 | 2279 | 3 | 5 | 8 | 11 | 13 | 16 | 18 | 21 | 24 |
| 17 | 2304 | 2330 | 2355 | 2380 | 2405 | 2430 | 2455 | 2480 | 2504 | 2529 | 2 | 5 | 7 | 10 | 12 | 15 | 17 | 20 | 22 |
| 18 | 2553 | 2577 | 2601 | 2625 | 2648 | 2672 | 2695 | 2718 | 2742 | 2765 | 2 | 5 | 7 | 9 | 12 | 14 | 16 | 19 | 21 |
| 19 | 2788 | 2810 | 2833 | 2856 | 2878 | 2900 | 2923 | 2945 | 2967 | 2989 | 2 | 4 | 7 | 9 | 11 | 13 | 16 | 18 | 20 |
| **20** | 3010 | 3032 | 3054 | 3075 | 3096 | 3118 | 3139 | 3160 | 3181 | 3201 | 2 | 4 | 6 | 8 | 11 | 13 | 15 | 17 | 19 |
| 21 | 3222 | 3243 | 3263 | 3284 | 3304 | 3324 | 3345 | 3365 | 3385 | 3404 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 |
| 22 | 3424 | 3444 | 3464 | 3483 | 3502 | 3522 | 3541 | 3560 | 3579 | 3598 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 17 |
| 23 | 3617 | 3636 | 3655 | 3674 | 3692 | 3711 | 3729 | 3747 | 3766 | 3784 | 2 | 4 | 6 | 7 | 9 | 11 | 13 | 15 | 17 |
| 24 | 3802 | 3820 | 3838 | 3856 | 3874 | 3892 | 3909 | 3927 | 3945 | 3962 | 2 | 4 | 5 | 7 | 9 | 11 | 12 | 14 | 16 |
| 25 | 3979 | 3997 | 4014 | 4031 | 4048 | 4065 | 4082 | 4099 | 4116 | 4133 | 2 | 4 | 5 | 7 | 9 | 10 | 12 | 14 | 16 |
| 26 | 4150 | 4166 | 4183 | 4200 | 4216 | 4232 | 4249 | 4265 | 4281 | 4298 | 2 | 3 | 5 | 7 | 8 | 10 | 11 | 13 | 15 |
| 27 | 4314 | 4330 | 4346 | 4362 | 4378 | 4393 | 4409 | 4425 | 4440 | 4456 | 2 | 3 | 5 | 6 | 8 | 9 | 11 | 12 | 14 |
| 28 | 4472 | 4487 | 4502 | 4518 | 4533 | 4548 | 4564 | 4579 | 4594 | 4609 | 2 | 3 | 5 | 6 | 8 | 9 | 11 | 12 | 14 |
| 29 | 4624 | 4639 | 4654 | 4669 | 4683 | 4698 | 4713 | 4728 | 4742 | 4757 | 1 | 3 | 4 | 6 | 7 | 9 | 10 | 12 | 13 |
| **30** | 4771 | 4786 | 4800 | 4814 | 4829 | 4843 | 4857 | 4871 | 4886 | 4900 | 1 | 3 | 4 | 6 | 7 | 9 | 10 | 11 | 13 |
| 31 | 4914 | 4928 | 4942 | 4955 | 4969 | 4983 | 4997 | 5011 | 5024 | 5038 | 1 | 3 | 4 | 5 | 7 | 8 | 10 | 11 | 12 |
| 32 | 5051 | 5065 | 5079 | 5092 | 5105 | 5119 | 5132 | 5145 | 5159 | 5172 | 1 | 3 | 4 | 5 | 7 | 8 | 9 | 11 | 12 |
| 33 | 5185 | 5198 | 5211 | 5224 | 5237 | 5250 | 5263 | 5276 | 5289 | 5302 | 1 | 3 | 4 | 5 | 7 | 8 | 9 | 11 | 12 |
| 34 | 5315 | 5328 | 5340 | 5353 | 5366 | 5378 | 5391 | 5403 | 5416 | 5428 | 1 | 2 | 4 | 5 | 6 | 8 | 9 | 10 | 11 |
| 35 | 5441 | 5453 | 5465 | 5478 | 5490 | 5502 | 5514 | 5527 | 5539 | 5551 | 1 | 2 | 4 | 5 | 6 | 7 | 9 | 10 | 11 |
| 36 | 5563 | 5575 | 5587 | 5599 | 5611 | 5623 | 5635 | 5647 | 5658 | 5670 | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 10 | 11 |
| 37 | 5682 | 5694 | 5705 | 5717 | 5729 | 5740 | 5752 | 5763 | 5775 | 5786 | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 9 | 11 |
| 38 | 5798 | 5809 | 5821 | 5832 | 5843 | 5855 | 5866 | 5877 | 5888 | 5899 | 1 | 2 | 3 | 5 | 6 | 7 | 8 | 9 | 10 |
| 39 | 5911 | 5922 | 5933 | 5944 | 5955 | 5966 | 5977 | 5988 | 5999 | 6010 | 1 | 2 | 3 | 4 | 5 | 7 | 8 | 9 | 10 |
| **40** | 6021 | 6031 | 6042 | 6053 | 6064 | 6075 | 6085 | 6096 | 6107 | 6117 | 1 | 2 | 3 | 4 | 5 | 6 | 8 | 9 | 10 |
| 41 | 6128 | 6138 | 6149 | 6160 | 6170 | 6180 | 6191 | 6201 | 6212 | 6222 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 42 | 6232 | 6243 | 6253 | 6263 | 6274 | 6284 | 6294 | 6304 | 6314 | 6325 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 43 | 6335 | 6345 | 6355 | 6365 | 6375 | 6385 | 6395 | 6405 | 6415 | 6425 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 44 | 6435 | 6444 | 6454 | 6464 | 6474 | 6484 | 6493 | 6503 | 6513 | 6522 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 45 | 6532 | 6542 | 6551 | 6561 | 6571 | 6580 | 6590 | 6599 | 6609 | 6618 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 46 | 6628 | 6637 | 6646 | 6656 | 6665 | 6675 | 6684 | 6693 | 6702 | 6712 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 7 | 8 |
| 47 | 6721 | 6730 | 6739 | 6749 | 6758 | 6767 | 6776 | 6785 | 6794 | 6803 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 7 | 8 |
| 48 | 6812 | 6821 | 6830 | 6839 | 6848 | 6857 | 6866 | 6875 | 6884 | 6893 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 7 | 8 |
| 49 | 6902 | 6911 | 6920 | 6928 | 6937 | 6946 | 6955 | 6964 | 6972 | 6981 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 | 8 |
| **50** | 6990 | 6998 | 7007 | 7016 | 7024 | 7033 | 7042 | 7050 | 7059 | 7067 | 1 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 |
| 51 | 7076 | 7084 | 7093 | 7101 | 7110 | 7118 | 7126 | 7135 | 7143 | 7152 | 1 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 |
| 52 | 7160 | 7168 | 7177 | 7185 | 7193 | 7202 | 7210 | 7218 | 7226 | 7235 | 1 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 7 |
| 53 | 7243 | 7251 | 7259 | 7267 | 7275 | 7284 | 7292 | 7300 | 7308 | 7316 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| 54 | 7324 | 7332 | 7340 | 7348 | 7356 | 7364 | 7372 | 7380 | 7388 | 7396 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| **N** | **0** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |

The proportional parts are stated in full for every tenth at the right-hand side. The logarithm of any number of four significant figures can be read directly by add-

## Table 25. Four Place Logarithms

| N | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **55** | 7404 | 7412 | 7419 | 7427 | 7435 | 7443 | 7451 | 7459 | 7466 | 7474 | 1 | 2 | 2 | 3 | 4 | 5 | 5 | 6 | 7 |
| 56 | 7482 | 7490 | 7497 | 7505 | 7513 | 7520 | 7528 | 7536 | 7543 | 7551 | 1 | 2 | 2 | 3 | 4 | 5 | 5 | 6 | 7 |
| 57 | 7559 | 7566 | 7574 | 7582 | 7589 | 7597 | 7604 | 7612 | 7619 | 7627 | 1 | 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 |
| 58 | 7634 | 7642 | 7649 | 7657 | 7664 | 7672 | 7679 | 7686 | 7694 | 7701 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 |
| 59 | 7709 | 7716 | 7723 | 7731 | 7738 | 7745 | 7752 | 7760 | 7767 | 7774 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 |
| **60** | 7782 | 7789 | 7796 | 7803 | 7810 | 7818 | 7825 | 7832 | 7839 | 7846 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |
| 61 | 7853 | 7860 | 7868 | 7875 | 7882 | 7889 | 7896 | 7903 | 7910 | 7917 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 6 | 6 |
| 62 | 7924 | 7931 | 7938 | 7945 | 7952 | 7959 | 7966 | 7973 | 7980 | 7987 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| 63 | 7993 | 8000 | 8007 | 8014 | 8021 | 8028 | 8035 | 8041 | 8048 | 8055 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| 64 | 8062 | 8069 | 8075 | 8082 | 8089 | 8096 | 8102 | 8109 | 8116 | 8122 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| **65** | 8129 | 8136 | 8142 | 8149 | 8156 | 8162 | 8169 | 8176 | 8182 | 8189 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| 66 | 8195 | 8202 | 8209 | 8215 | 8222 | 8228 | 8235 | 8241 | 8248 | 8254 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| 67 | 8261 | 8267 | 8274 | 8280 | 8287 | 8293 | 8299 | 8306 | 8312 | 8319 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| 68 | 8325 | 8331 | 8338 | 8344 | 8351 | 8357 | 8363 | 8370 | 8376 | 8382 | 1 | 1 | 2 | 3 | 3 | 4 | 4 | 5 | 6 |
| 69 | 8388 | 8395 | 8401 | 8407 | 8414 | 8420 | 8426 | 8432 | 8439 | 8445 | 1 | 1 | 2 | 3 | 3 | 4 | 4 | 5 | 6 |
| **70** | 8451 | 8457 | 8463 | 8470 | 8476 | 8482 | 8488 | 8494 | 8500 | 8506 | 1 | 1 | 2 | 3 | 3 | 4 | 4 | 5 | 6 |
| 71 | 8513 | 8519 | 8525 | 8531 | 8537 | 8543 | 8549 | 8555 | 8561 | 8567 | 1 | 1 | 2 | 3 | 3 | 4 | 4 | 5 | 6 |
| 72 | 8573 | 8579 | 8585 | 8591 | 8597 | 8603 | 8609 | 8615 | 8621 | 8627 | 1 | 1 | 2 | 3 | 3 | 4 | 4 | 5 | 6 |
| 73 | 8633 | 8639 | 8645 | 8651 | 8657 | 8663 | 8669 | 8675 | 8681 | 8686 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 74 | 8692 | 8698 | 8704 | 8710 | 8716 | 8722 | 8727 | 8733 | 8739 | 8745 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| 75 | 8751 | 8756 | 8762 | 8768 | 8774 | 8779 | 8785 | 8791 | 8797 | 8802 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 5 |
| 76 | 8808 | 8814 | 8820 | 8825 | 8831 | 8837 | 8842 | 8848 | 8854 | 8859 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 77 | 8865 | 8871 | 8876 | 8882 | 8887 | 8893 | 8899 | 8904 | 8910 | 8915 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 78 | 8921 | 8927 | 8932 | 8938 | 8943 | 8949 | 8954 | 8960 | 8965 | 8971 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 79 | 8976 | 8982 | 8987 | 8993 | 8998 | 9004 | 9009 | 9015 | 9020 | 9025 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| **80** | 9031 | 9036 | 9042 | 9047 | 9053 | 9058 | 9063 | 9069 | 9074 | 9079 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 81 | 9085 | 9090 | 9096 | 9101 | 9106 | 9112 | 9117 | 9122 | 9128 | 9133 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 82 | 9138 | 9143 | 9149 | 9154 | 9159 | 9165 | 9170 | 9175 | 9180 | 9186 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 83 | 9191 | 9196 | 9201 | 9206 | 9212 | 9217 | 9222 | 9227 | 9232 | 9238 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 84 | 9243 | 9248 | 9253 | 9258 | 9263 | 9269 | 9274 | 9279 | 9284 | 9289 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| **85** | 9294 | 9299 | 9304 | 9309 | 9315 | 9320 | 9325 | 9330 | 9335 | 9340 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 86 | 9345 | 9350 | 9355 | 9360 | 9365 | 9370 | 9375 | 9380 | 9385 | 9390 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 87 | 9395 | 9400 | 9405 | 9410 | 9415 | 9420 | 9425 | 9430 | 9435 | 9440 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| 88 | 9445 | 9450 | 9455 | 9460 | 9465 | 9469 | 9474 | 9479 | 9484 | 9489 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 89 | 9494 | 9499 | 9504 | 9509 | 9513 | 9518 | 9523 | 9528 | 9533 | 9538 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| **90** | 9542 | 9547 | 9552 | 9557 | 9562 | 9566 | 9571 | 9576 | 9581 | 9586 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 91 | 9590 | 9595 | 9600 | 9605 | 9609 | 9614 | 9619 | 9624 | 9628 | 9633 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 92 | 9638 | 9643 | 9647 | 9652 | 9657 | 9661 | 9666 | 9671 | 9675 | 9680 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 93 | 9685 | 9689 | 9694 | 9699 | 9703 | 9708 | 9713 | 9717 | 9722 | 9727 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 94 | 9731 | 9736 | 9741 | 9745 | 9750 | 9754 | 9759 | 9763 | 9768 | 9773 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| **95** | 9777 | 9782 | 9786 | 9791 | 9795 | 9800 | 9805 | 9809 | 9814 | 9818 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 96 | 9823 | 9827 | 9832 | 9836 | 9841 | 9845 | 9850 | 9854 | 9859 | 9863 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 97 | 9868 | 9872 | 9877 | 9881 | 9886 | 9890 | 9894 | 9899 | 9903 | 9908 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| 98 | 9912 | 9917 | 9921 | 9926 | 9930 | 9934 | 9939 | 9943 | 9948 | 9952 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 3 | 4 |
| 99 | 9956 | 9961 | 9965 | 9969 | 9974 | 9978 | 9983 | 9987 | 9991 | 9996 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 3 | 4 |
| **N** | **0** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |

ing the proportional part corresponding to the fourth figure to the tabular number corresponding to the first three figures. There may be an error of 1 in the last place.

## TABLE 26. ANTILOGARITHMS TO FOUR PLACES

| | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **.00** | 1000 | 1002 | 1005 | 1007 | 1009 | 1012 | 1014 | 1016 | 1019 | 1021 | 0 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 |
| .01 | 1023 | 1026 | 1028 | 1030 | 1033 | 1035 | 1038 | 1040 | 1042 | 1045 | 0 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 |
| .02 | 1047 | 1050 | 1052 | 1054 | 1057 | 1059 | 1062 | 1064 | 1067 | 1069 | 0 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 |
| .03 | 1072 | 1074 | 1076 | 1079 | 1081 | 1084 | 1086 | 1089 | 1091 | 1094 | 0 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 |
| .04 | 1096 | 1099 | 1102 | 1104 | 1107 | 1109 | 1112 | 1114 | 1117 | 1119 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 |
| .05 | 1122 | 1125 | 1127 | 1130 | 1132 | 1135 | 1138 | 1140 | 1143 | 1146 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 |
| .06 | 1148 | 1151 | 1153 | 1156 | 1159 | 1161 | 1164 | 1167 | 1169 | 1172 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 |
| .07 | 1175 | 1178 | 1180 | 1183 | 1186 | 1189 | 1191 | 1194 | 1197 | 1199 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 |
| .08 | 1202 | 1205 | 1208 | 1211 | 1213 | 1216 | 1219 | 1222 | 1225 | 1227 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 3 |
| .09 | 1230 | 1233 | 1236 | 1239 | 1242 | 1245 | 1247 | 1250 | 1253 | 1256 | 0 | | | 1 | 1 | 2 | 2 | 2 | 3 |
| **.10** | 1259 | 1262 | 1265 | 1268 | 1271 | 1274 | 1276 | 1279 | 1282 | 1285 | 0 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 3 |
| .11 | 1288 | 1291 | 1294 | 1297 | 1300 | 1303 | 1306 | 1309 | 1312 | 1315 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| .12 | 1318 | 1321 | 1324 | 1327 | 1330 | 1334 | 1337 | 1340 | 1343 | 1346 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 3 |
| .13 | 1349 | 1352 | 1355 | 1358 | 1361 | 1365 | 1368 | 1371 | 1374 | 1377 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 3 | 3 |
| .14 | 1380 | 1384 | 1387 | 1390 | 1393 | 1396 | 1400 | 1403 | 1406 | 1409 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 3 | 3 |
| .15 | 1413 | 1416 | 1419 | 1422 | 1426 | 1429 | 1432 | 1435 | 1439 | 1442 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 3 | 3 |
| .16 | 1445 | 1449 | 1452 | 1455 | 1459 | 1462 | 1466 | 1469 | 1472 | 1476 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 3 | 3 |
| .17 | 1479 | 1483 | 1486 | 1489 | 1493 | 1496 | 1500 | 1503 | 1507 | 1510 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 3 | 3 |
| .18 | 1514 | 1517 | 1521 | 1524 | 1528 | 1531 | 1535 | 1538 | 1542 | 1545 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 3 | 3 |
| .19 | 1549 | 1552 | 1556 | 1560 | 1563 | 1567 | 1570 | 1574 | 1578 | 1581 | 0 | 1 | 1 | 1 | 2 | 2 | 2 | 3 | 3 |
| **.20** | 1585 | 1589 | 1592 | 1596 | 1600 | 1603 | 1607 | 1611 | 1614 | 1618 | 0 | 1 | 1 | 1 | 2 | 2 | 3 | 3 | 3 |
| .21 | 1622 | 1626 | 1629 | 1633 | 1637 | 1641 | 1644 | 1648 | 1652 | 1656 | 0 | 1 | 1 | 1 | 2 | 2 | 3 | 3 | 3 |
| .22 | 1660 | 1663 | 1667 | 1671 | 1675 | 1679 | 1683 | 1687 | 1690 | 1694 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 3 |
| .23 | 1698 | 1702 | 1706 | 1710 | 1714 | 1718 | 1722 | 1726 | 1730 | 1734 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| .24 | 1738 | 1742 | 1746 | 1750 | 1754 | 1758 | 1762 | 1766 | 1770 | 1774 | 0 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 4 |
| .25 | 1778 | 1782 | 1786 | 1791 | 1795 | 1799 | 1803 | 1807 | 1811 | 1816 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 3 | 4 |
| .26 | 1820 | 1824 | 1828 | 1832 | 1837 | 1841 | 1845 | 1849 | 1854 | 1858 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 3 | 4 |
| .27 | 1862 | 1866 | 1871 | 1875 | 1879 | 1884 | 1888 | 1892 | 1897 | 1901 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 3 | 4 |
| .28 | 1905 | 1910 | 1914 | 1919 | 1923 | 1928 | 1932 | 1936 | 1941 | 1945 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| .29 | 1950 | 1954 | 1959 | 1963 | 1968 | 1972 | 1977 | 1982 | 1986 | 1991 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| **.30** | 1995 | 2000 | 2004 | 2009 | 2014 | 2018 | 2023 | 2028 | 2032 | 2037 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| .31 | 2042 | 2046 | 2051 | 2056 | 2061 | 2065 | 2070 | 2075 | 2080 | 2084 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| .32 | 2089 | 2094 | 2099 | 2104 | 2109 | 2113 | 2118 | 2123 | 2128 | 2133 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| .33 | 2138 | 2143 | 2148 | 2153 | 2158 | 2163 | 2168 | 2173 | 2178 | 2183 | 0 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 |
| .34 | 2188 | 2193 | 2198 | 2203 | 2208 | 2213 | 2218 | 2223 | 2228 | 2234 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| .35 | 2239 | 2244 | 2249 | 2254 | 2259 | 2265 | 2270 | 2275 | 2280 | 2286 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| .36 | 2291 | 2296 | 2301 | 2307 | 2312 | 2317 | 2323 | 2328 | 2333 | 2339 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| .37 | 2344 | 2350 | 2355 | 2360 | 2366 | 2371 | 2377 | 2382 | 2388 | 2393 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 4 | 5 |
| .38 | 2399 | 2404 | 2410 | 2415 | 2421 | 2427 | 2432 | 2438 | 2443 | 2449 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 5 |
| .39 | 2455 | 2460 | 2466 | 2472 | 2477 | 2483 | 2489 | 2495 | 2500 | 2506 | 1 | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 5 |
| **.40** | 2512 | 2518 | 2523 | 2529 | 2535 | 2541 | 2547 | 2553 | 2559 | 2564 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| .41 | 2570 | 2576 | 2582 | 2588 | 2594 | 2600 | 2606 | 2612 | 2618 | 2624 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 5 |
| .42 | 2630 | 2636 | 2642 | 2649 | 2655 | 2661 | 2667 | 2673 | 2679 | 2685 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 6 |
| .43 | 2692 | 2698 | 2704 | 2710 | 2716 | 2723 | 2729 | 2735 | 2742 | 2748 | 1 | 1 | 2 | 2 | 3 | 4 | 4 | 5 | 6 |
| .44 | 2754 | 2761 | 2767 | 2773 | 2780 | 2786 | 2793 | 2799 | 2805 | 2812 | 1 | 1 | 2 | 3 | 3 | 4 | 4 | 5 | 6 |
| .45 | 2818 | 2825 | 2831 | 2838 | 2844 | 2851 | 2858 | 2864 | 2871 | 2877 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| .46 | 2884 | 2891 | 2897 | 2904 | 2911 | 2917 | 2924 | 2931 | 2938 | 2944 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| .47 | 2951 | 2958 | 2965 | 2972 | 2979 | 2985 | 2992 | 2999 | 3006 | 3013 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 5 | 6 |
| .48 | 3020 | 3027 | 3034 | 3041 | 3048 | 3055 | 3062 | 3069 | 3076 | 3083 | 1 | 1 | 2 | 3 | 3 | 4 | 5 | 6 | 6 |
| .49 | 3090 | 3097 | 3105 | 3112 | 3119 | 3126 | 3133 | 3141 | 3148 | 3155 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 6 |

## TABLE 26. ANTILOGARITHMS TO FOUR PLACES

| | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| .50 | 3162 | 3170 | 3177 | 3184 | 3192 | 3199 | 3206 | 3214 | 3221 | 3228 | 1 | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 |
| .51 | 3236 | 3243 | 3251 | 3258 | 3266 | 3273 | 3281 | 3289 | 3296 | 3304 | 1 | 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 |
| .52 | 3311 | 3319 | 3327 | 3334 | 3342 | 3350 | 3357 | 3365 | 3373 | 3381 | 1 | 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 |
| .53 | 3388 | 3396 | 3404 | 3412 | 3420 | 3428 | 3436 | 3443 | 3451 | 3459 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| .54 | 3467 | 3475 | 3483 | 3491 | 3499 | 3508 | 3516 | 3524 | 3532 | 3540 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 6 | 7 |
| .55 | 3548 | 3556 | 3565 | 3573 | 3581 | 3589 | 3597 | 3606 | 3614 | 3622 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 7 | 7 |
| .56 | 3631 | 3639 | 3648 | 3656 | 3664 | 3673 | 3681 | 3690 | 3698 | 3707 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| .57 | 3715 | 3724 | 3733 | 3741 | 3750 | 3758 | 3767 | 3776 | 3784 | 3793 | 1 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 |
| .58 | 3802 | 3811 | 3819 | 3828 | 3837 | 3846 | 3855 | 3864 | 3873 | 3882 | 1 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 |
| .59 | 3890 | 3899 | 3908 | 3917 | 3926 | 3936 | 3945 | 3954 | 3963 | 3972 | 1 | 2 | 3 | 4 | 5 | 5 | 6 | 7 | 8 |
| .60 | 3981 | 3990 | 3999 | 4009 | 4018 | 4027 | 4036 | 4046 | 4055 | 4064 | 1 | 2 | 3 | 4 | 5 | 6 | 6 | 7 | 8 |
| .61 | 4074 | 4083 | 4093 | 4102 | 4111 | 4121 | 4130 | 4140 | 4150 | 4159 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| .62 | 4169 | 4178 | 4188 | 4198 | 4207 | 4217 | 4227 | 4236 | 4246 | 4256 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| .63 | 4266 | 4276 | 4285 | 4295 | 4305 | 4315 | 4325 | 4335 | 4345 | 4355 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| .64 | 4365 | 4375 | 4385 | 4395 | 4406 | 4416 | 4426 | 4436 | 4446 | 4457 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| .65 | 4467 | 4477 | 4487 | 4498 | 4508 | 4519 | 4529 | 4539 | 4550 | 4560 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| .66 | 4571 | 4581 | 4592 | 4603 | 4613 | 4624 | 4634 | 4645 | 4656 | 4667 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 9 | 10 |
| .67 | 4677 | 4688 | 4699 | 4710 | 4721 | 4732 | 4742 | 4753 | 4764 | 4775 | 1 | 2 | 3 | 4 | 5 | 7 | 8 | 9 | 10 |
| .68 | 4786 | 4797 | 4808 | 4819 | 4831 | 4842 | 4853 | 4864 | 4875 | 4887 | 1 | 2 | 3 | 5 | 6 | 7 | 8 | 9 | 10 |
| .69 | 4898 | 4909 | 4920 | 4932 | 4943 | 4955 | 4966 | 4977 | 4989 | 5000 | 1 | 2 | 3 | 5 | 6 | 7 | 8 | 9 | 10 |
| .70 | 5012 | 5023 | 5035 | 5047 | 5058 | 5070 | 5082 | 5093 | 5105 | 5117 | 1 | 2 | 3 | 5 | 6 | 7 | 8 | 9 | 10 |
| .71 | 5129 | 5140 | 5152 | 5164 | 5176 | 5188 | 5200 | 5212 | 5224 | 5236 | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 10 | 11 |
| .72 | 5248 | 5260 | 5272 | 5284 | 5297 | 5309 | 5321 | 5333 | 5346 | 5358 | 1 | 2 | 4 | 5 | 6 | 7 | 9 | 10 | 11 |
| .73 | 5370 | 5383 | 5395 | 5408 | 5420 | 5433 | 5445 | 5458 | 5470 | 5483 | 1 | 3 | 4 | 5 | 6 | 8 | 9 | 10 | 11 |
| .74 | 5495 | 5508 | 5521 | 5534 | 5546 | 5559 | 5572 | 5585 | 5598 | 5610 | 1 | 3 | 4 | 5 | 6 | 8 | 9 | 10 | 12 |
| .75 | 5623 | 5636 | 5649 | 5662 | 5675 | 5689 | 5702 | 5715 | 5728 | 5741 | 1 | 3 | 4 | 5 | 7 | 8 | 9 | 11 | 12 |
| .76 | 5754 | 5768 | 5781 | 5794 | 5808 | 5821 | 5834 | 5848 | 5861 | 5875 | 1 | 3 | 4 | 5 | 7 | 8 | 9 | 11 | 12 |
| .77 | 5888 | 5902 | 5916 | 5929 | 5943 | 5957 | 5970 | 5984 | 5998 | 6012 | 1 | 3 | 4 | 5 | 7 | 8 | 10 | 11 | 12 |
| .78 | 6026 | 6039 | 6053 | 6067 | 6081 | 6095 | 6109 | 6124 | 6138 | 6152 | 1 | 3 | 4 | 6 | 7 | 8 | 10 | 11 | 13 |
| .79 | 6166 | 6180 | 6194 | 6209 | 6223 | 6237 | 6252 | 6266 | 6281 | 6295 | 1 | 3 | 4 | 6 | 7 | 9 | 10 | 11 | 13 |
| .80 | 6310 | 6324 | 6339 | 6353 | 6368 | 6383 | 6397 | 6412 | 6427 | 6442 | 1 | 3 | 4 | 6 | 7 | 9 | 10 | 12 | 13 |
| .81 | 6457 | 6471 | 6486 | 6501 | 6516 | 6531 | 6546 | 6561 | 6577 | 6592 | 2 | 3 | 5 | 6 | 8 | 9 | 11 | 12 | 14 |
| .82 | 6607 | 6622 | 6637 | 6653 | 6668 | 6683 | 6699 | 6714 | 6730 | 6745 | 2 | 3 | 5 | 6 | 8 | 9 | 11 | 12 | 14 |
| .83 | 6761 | 6776 | 6792 | 6808 | 6823 | 6839 | 6855 | 6871 | 6887 | 6902 | 2 | 3 | 5 | 6 | 8 | 9 | 11 | 13 | 14 |
| .84 | 6918 | 6934 | 6950 | 6966 | 6982 | 6998 | 7015 | 7031 | 7047 | 7063 | 2 | 3 | 5 | 7 | 8 | 10 | 11 | 13 | 15 |
| .85 | 7079 | 7096 | 7112 | 7129 | 7145 | 7161 | 7178 | 7194 | 7211 | 7228 | 2 | 3 | 5 | 7 | 8 | 10 | 12 | 13 | 15 |
| .86 | 7244 | 7261 | 7278 | 7295 | 7311 | 7328 | 7345 | 7362 | 7379 | 7396 | 2 | 3 | 5 | 7 | 8 | 10 | 12 | 14 | 15 |
| .87 | 7413 | 7430 | 7447 | 7464 | 7482 | 7499 | 7516 | 7534 | 7551 | 7568 | 2 | 4 | 5 | 7 | 9 | 10 | 12 | 14 | 16 |
| .88 | 7586 | 7603 | 7621 | 7638 | 7656 | 7674 | 7691 | 7709 | 7727 | 7745 | 2 | 4 | 5 | 7 | 9 | 11 | 12 | 14 | 16 |
| .89 | 7762 | 7780 | 7798 | 7816 | 7834 | 7852 | 7870 | 7889 | 7907 | 7925 | 2 | 4 | 6 | 7 | 9 | 11 | 13 | 14 | 16 |
| .90 | 7943 | 7962 | 7980 | 7998 | 8017 | 8035 | 8054 | 8072 | 8091 | 8110 | 2 | 4 | 6 | 7 | 9 | 11 | 13 | 15 | 17 |
| .91 | 8128 | 8147 | 8166 | 8185 | 8204 | 8222 | 8241 | 8260 | 8279 | 8299 | 2 | 4 | 6 | 8 | 9 | 11 | 13 | 15 | 17 |
| .92 | 8318 | 8337 | 8356 | 8375 | 8395 | 8414 | 8433 | 8453 | 8472 | 8492 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 15 | 17 |
| .93 | 8511 | 8531 | 8551 | 8570 | 8590 | 8610 | 8630 | 8650 | 8670 | 8690 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 |
| .94 | 8710 | 8730 | 8750 | 8770 | 8790 | 8810 | 8831 | 8851 | 8872 | 8892 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 |
| .95 | 8913 | 8933 | 8954 | 8974 | 8995 | 9016 | 9036 | 9057 | 9078 | 9099 | 2 | 4 | 6 | 8 | 10 | 12 | 15 | 17 | 19 |
| .96 | 9120 | 9141 | 9162 | 9183 | 9204 | 9226 | 9247 | 9268 | 9290 | 9311 | 2 | 4 | 6 | 9 | 11 | 13 | 15 | 17 | 19 |
| .97 | 9333 | 9354 | 9376 | 9397 | 9419 | 9441 | 9462 | 9484 | 9506 | 9528 | 2 | 4 | 6 | 9 | 11 | 13 | 15 | 17 | 20 |
| .98 | 9550 | 9572 | 9594 | 9616 | 9638 | 9661 | 9683 | 9705 | 9727 | 9750 | 2 | 4 | 7 | 9 | 11 | 13 | 16 | 18 | 20 |
| .99 | 9772 | 9795 | 9817 | 9840 | 9863 | 9886 | 9908 | 9931 | 9954 | 9977 | 2 | 5 | 7 | 9 | 11 | 14 | 16 | 18 | 20 |

TABLE 27. SHELF REAGENTS

| Reagent | Specific Gravity | Per cent by Weight | Approximate Normality |
|---|---|---|---|
| Acetic acid, Glacial | 1.05 | 99 $H_4C_2O_2$ | 17 |
| Ammonium hydroxide | 0.90 | 28 $NH_3$ | 15 |
| Ethyl alcohol | 0.80 | 95 $C_2H_6O$ | — |
| Hydrochloric acid | 1.19 | 39 HCl | 13 |
| Nitric acid | 1.42 | 71 $HNO_3$ | 16 |
| Sodium hydroxide, Satd. | 1.52 | 50 NaOH | 19 |
| Sulfuric acid | 1.84 | 96 $H_2SO_4$ | 36 |

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